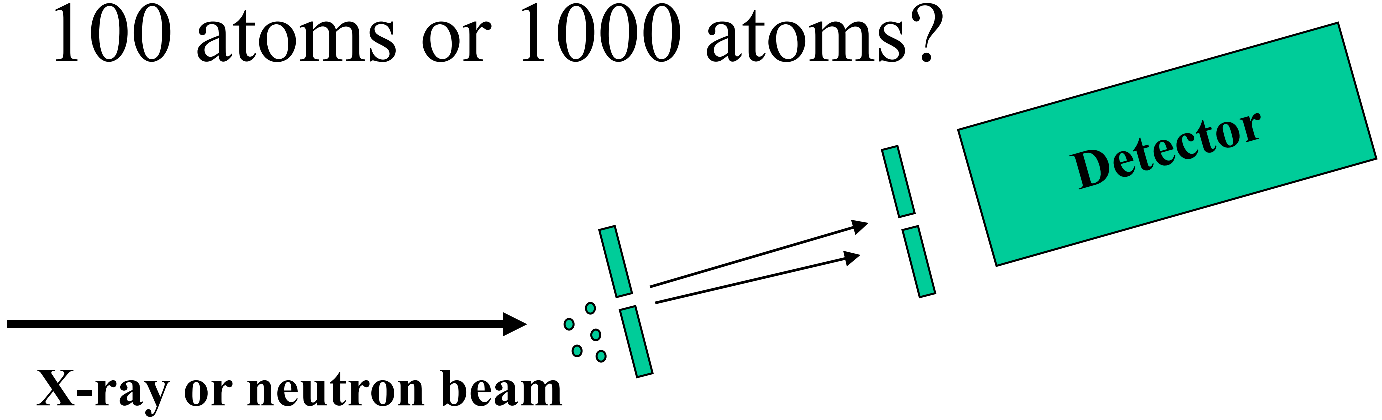
Diffuse Scattering

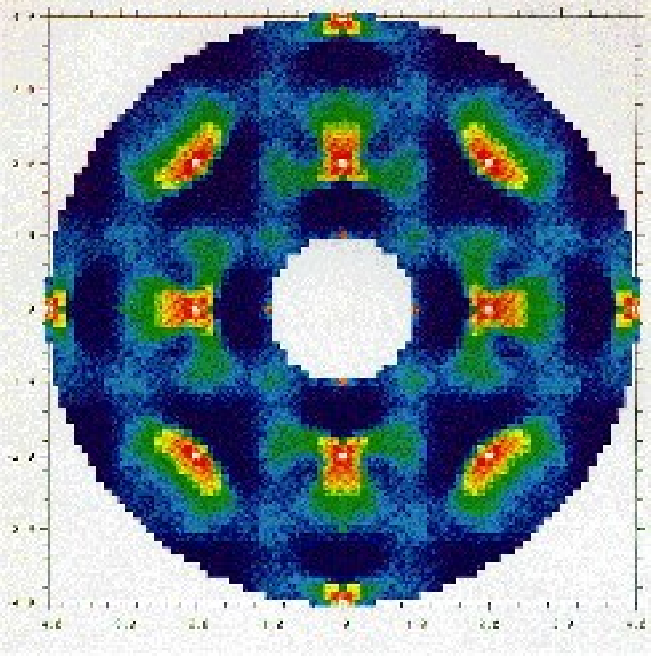
- Anticipatory (trick) question: If you have an x-ray or neutron detector looking at a small sample volume, which will scatter more x-rays or neutrons into the detector 1 atom 100 atoms or 1000 atoms?



Answer: Depends!

Diffuse Scattering

Gene E. Ice
Materials Science and Technology Division
Oak Ridge National Laboratory, USA



National School on Neutron and X-ray Scattering
ORNL/SNS August 2012

Presentation concentrates year graduate-level course into 1 hour

- Skip mathematical complexities
- Expose to range of applications
- Develop ***intuition*** for length scales
- Talk like x-ray/neutron scattering guru
  - ***Reciprocal space***
  - ***Debye Temperature***
  - ***Laue monotonic***
  - ***Krivoglaz defects of 1st/2nd kinds***!

Great for cocktail parties or impressing attractive strangers-

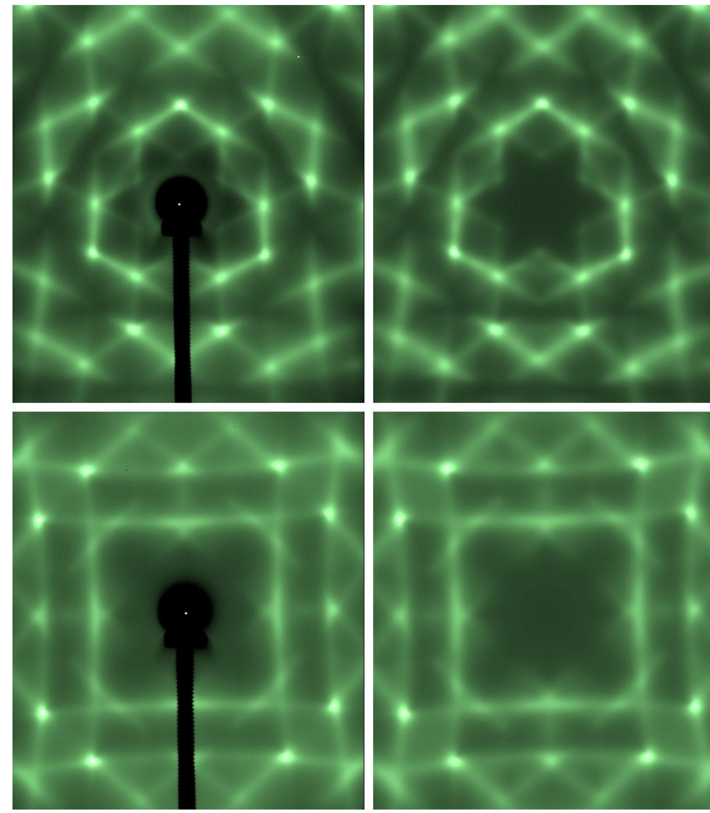
Important for recognizing origins of diffuse scattering!

Diffuse scattering poised for a revolution!

- Synchrotron sources /new tools enable new applications
  - Intensity for weak signals
  - High energy for simplified data analysis
  - Small (dangerous) samples

- Advanced neutron instruments emerging
  - Low Z elements
  - Magnetic scattering
  - Different contrast

- New theories provide direct link between experiments and first-principles calculations

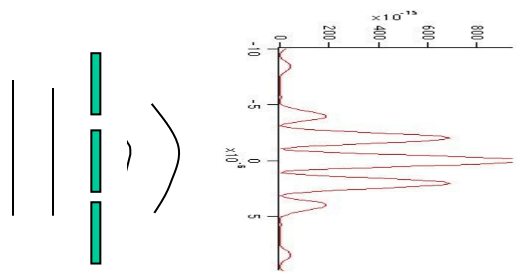


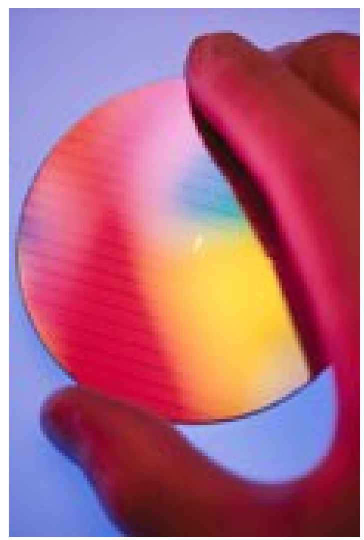
Experiment **Theory**

Major controversies have split leading scientists in once staid community!

What you already know- arrangement of atoms redistributes scattering

- Familiar light example
- Practical applications- zero background plates for powder diffraction
- Wave→diffraction

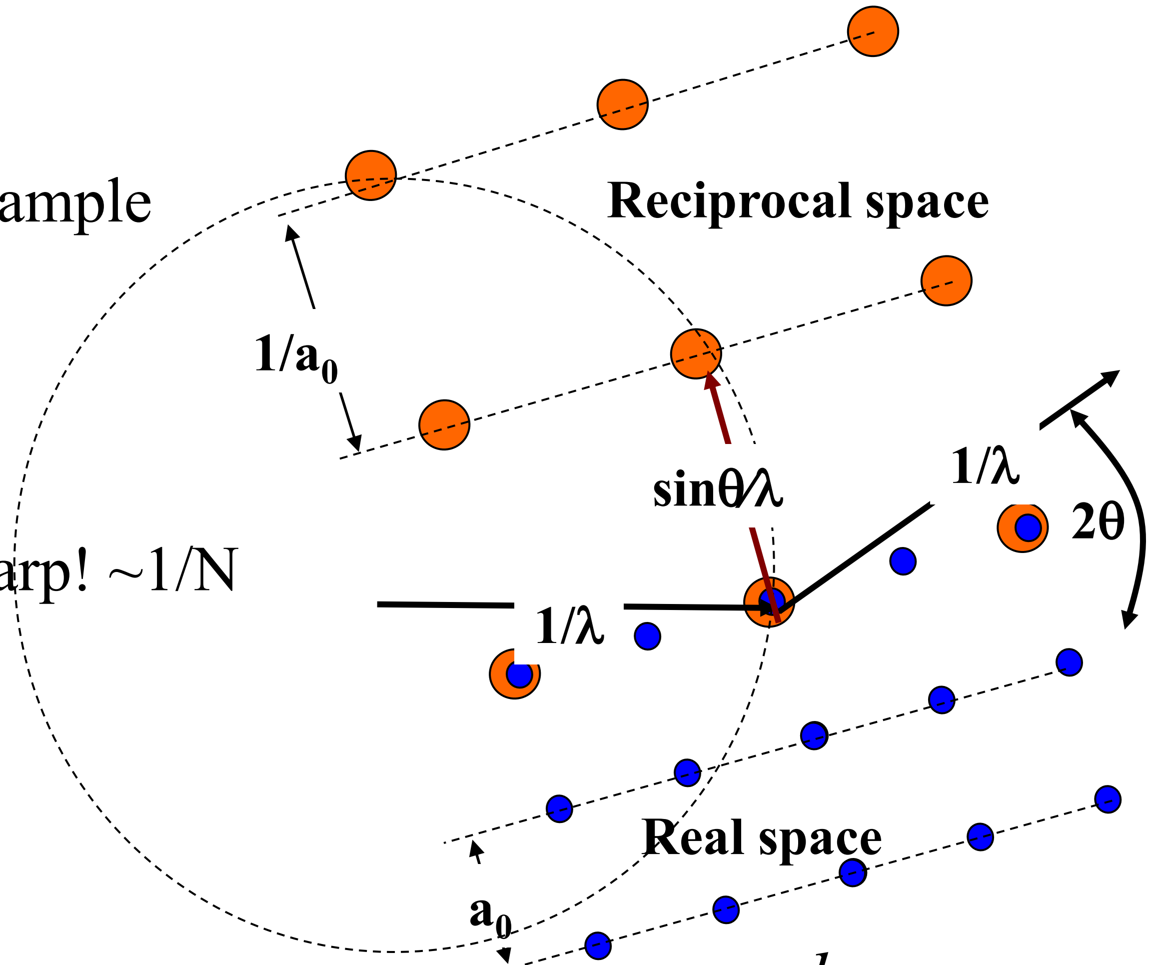




X-ray or neutron beam

You already know that Bragg reflections occur when scattering amplitudes add *constructively*

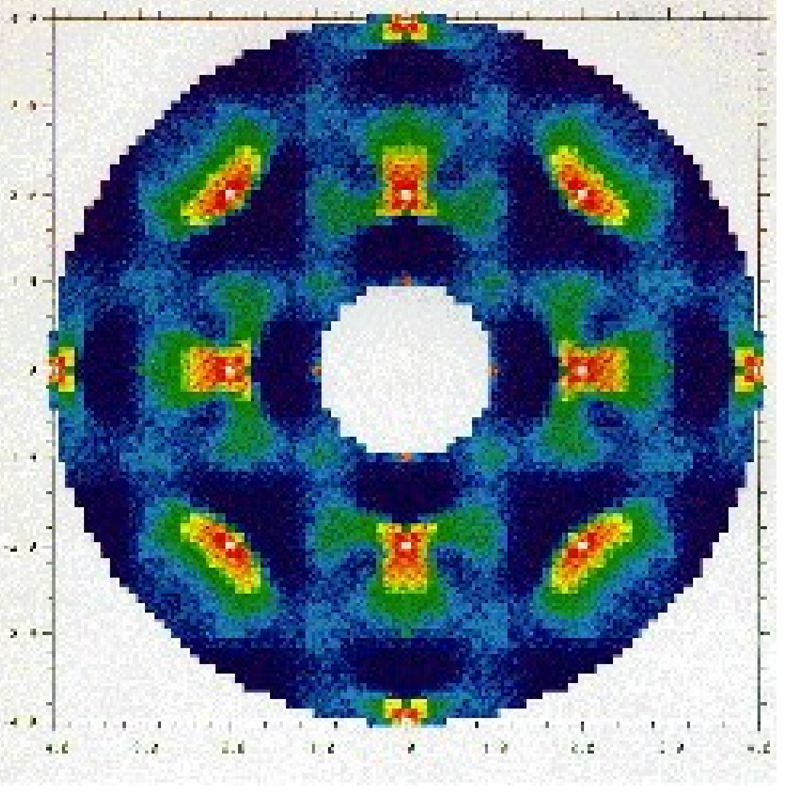
- Orientation of sample
- Wavelength
- Bragg Peaks sharp! ~1/N (arc seconds)



Think in terms of *momentum transfer* $\bar{p}_0 = \dfrac{h}{\lambda}\hat{d}_0$

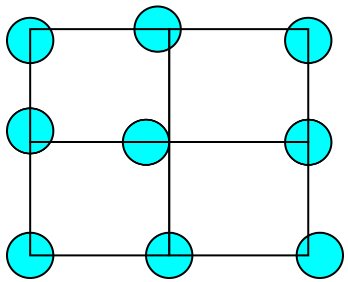
If crystal lattice of atoms leads to Bragg peaks-what happens when an atom is out of place/missing?

- Weakens Bragg peaks
- Redistributes scattering intensity in reciprocal space

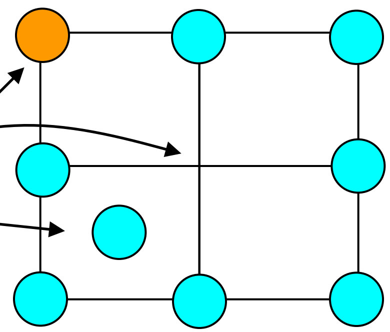


Diffuse scattering due to *local* (short ranged) correlations/ fluctuations

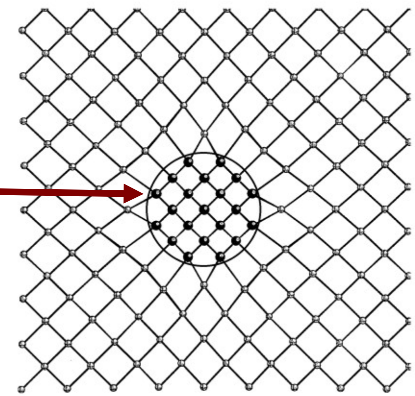
- Thermal diffuse scattering (TDS)



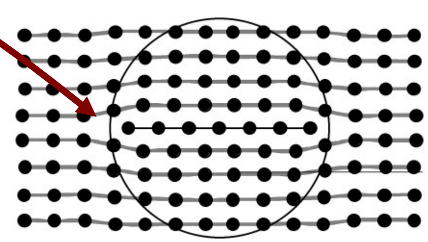
- Point defect
  - Site substitution
  - Vacancy
  - Interstitial



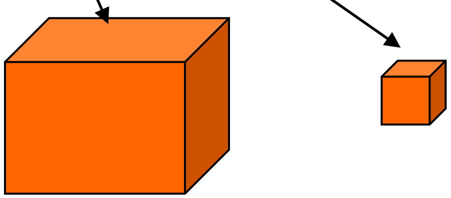
- Precipitate



- Dislocations



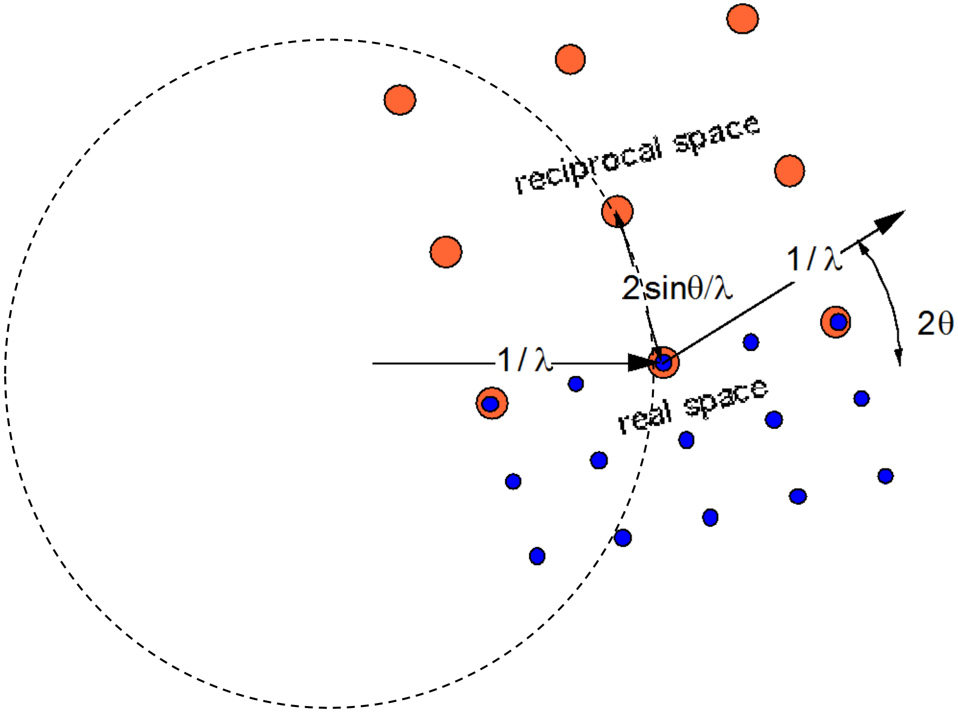
- Truncated surface- more



All have in common reduced correlation length!

You already know length scales are inverted!

- Big real→small reciprocal
- Small real→big reciprocal
- ***Same behavior for correlation length scales***
  - Long real-space correlation lengths scattering close to Bragg peaks

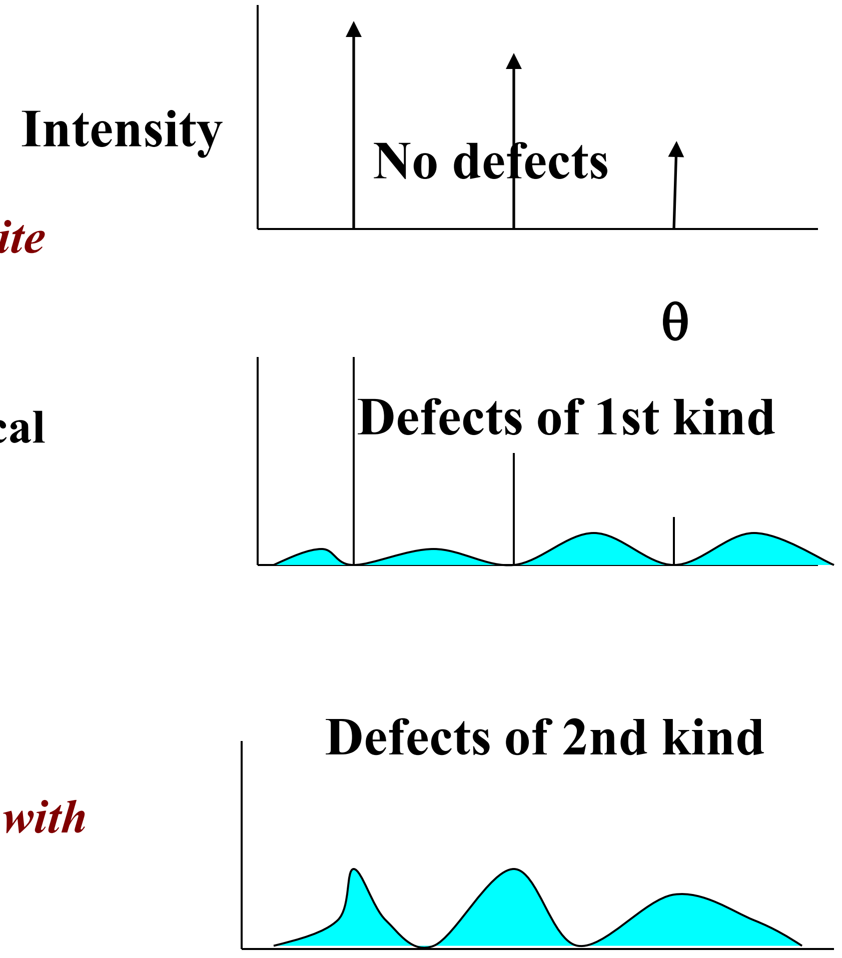


If you remember nothing else!

Krivoglaz classified defects by effect on Bragg Peak

- **Defects of 1st kind**
  - *Atomic displacements remain finite*
  - **Bragg width unchanged**
  - **Bragg intensity decreased**
  - **Diffuse redistributed in reciprocal space**

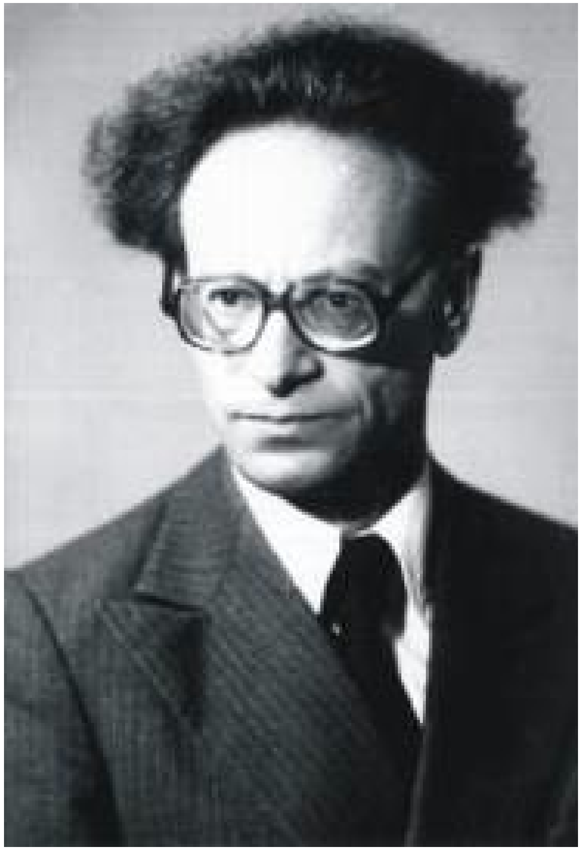
- **Defects of 2nd kind**
  - **No longer distinct Bragg peaks**
  - *Displacements continue to grow with crystal size*



Who the heck was Krivoglaz?

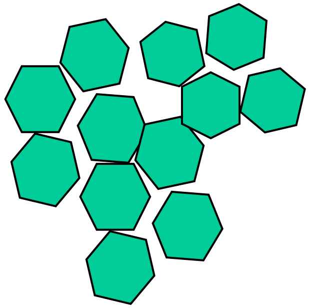
- Brilliant Ukrainian scientist
- Dissertation –predated Mossbauer’s work

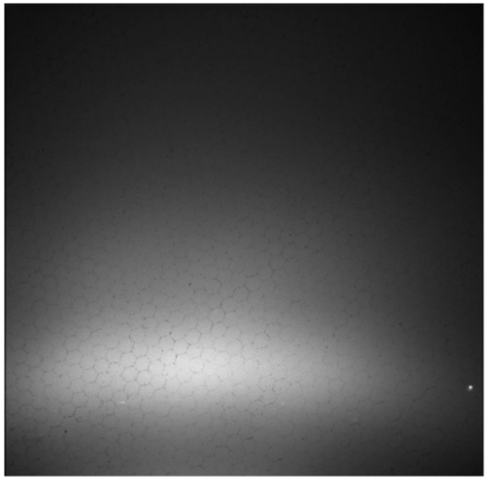
- Pioneered a general way of categorizing and studying defects using x-rays/neutrons



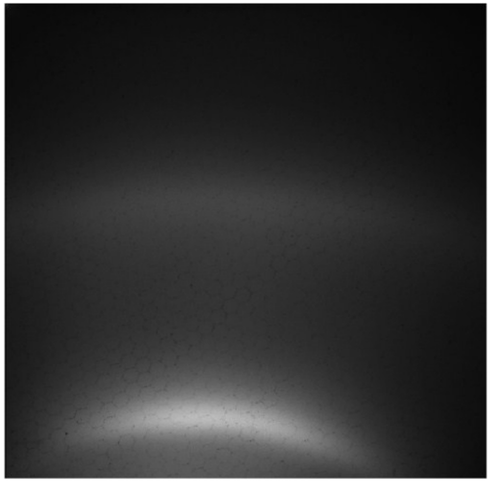
Dimensionality Krivoglaz defect of second kind- influences diffraction

- **Small size→broad diffraction**
- **Polycrystalline**

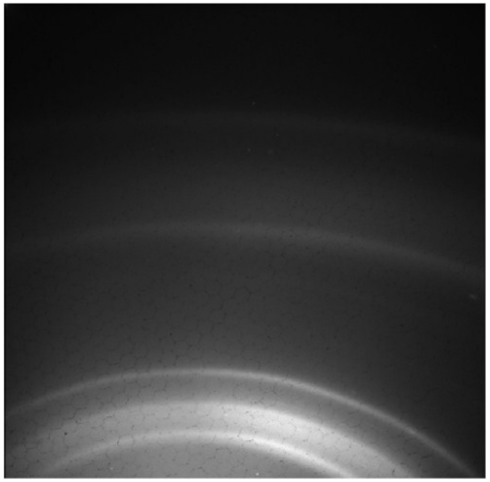




a. Amorphous



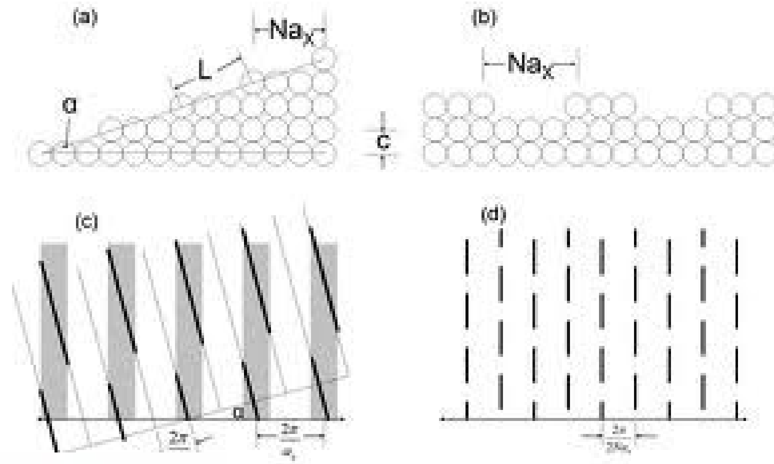
b. nanocrystalline

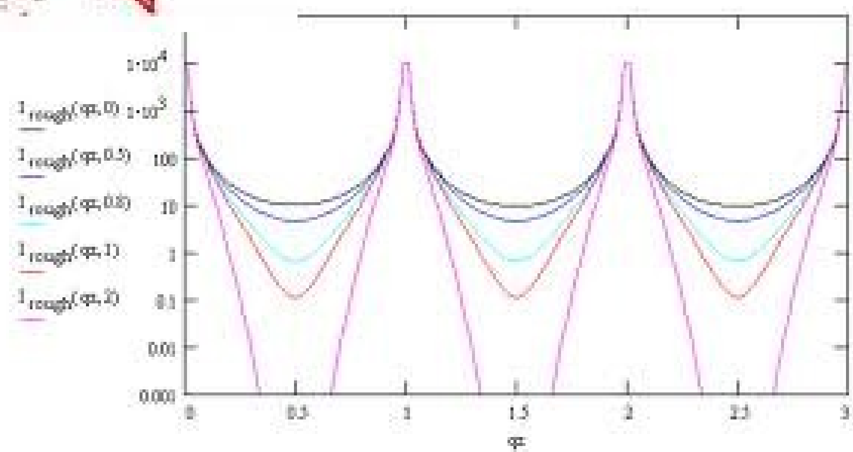


c. crystalline

Single crystals and surfaces -truncation rods

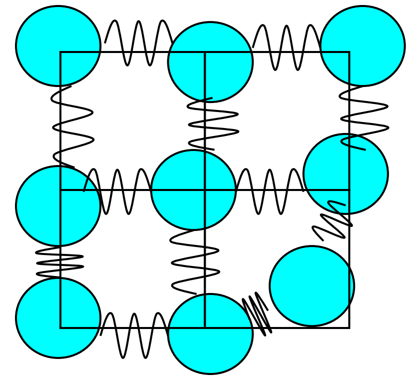
- Diffuse scattering perpendicular to surface
- Connect to Bragg Peaks
- Intensity falloff indicates roughness
  - Slow (smooth)
  - Fast (rough)

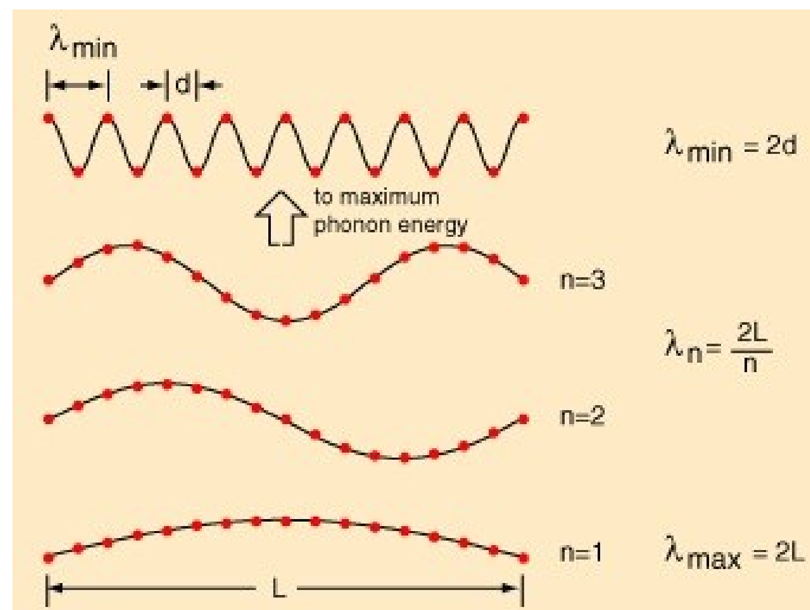




Thermal motion-Temperature Diffuse Scattering-(TDS) -defect of 1st kind

- Atoms coupled through atomic bonding
- Uncorrelated displacements at distant sites
  - (finite)
- Phonons (wave description)
  - Amplitude
  - Period
  - Propagation direction
  - Polarization (transverse/compressional)





Sophisticated theories from James, Born Von Karmen, Krivoglaz

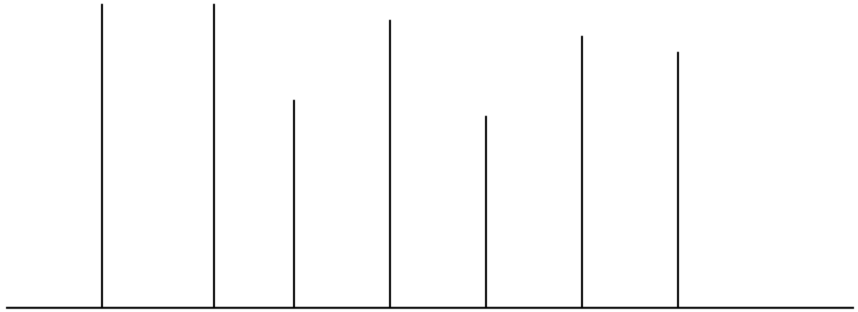
A little math helps for party conversation

- Decrease in Bragg intensity scales like e^{-2M}, where

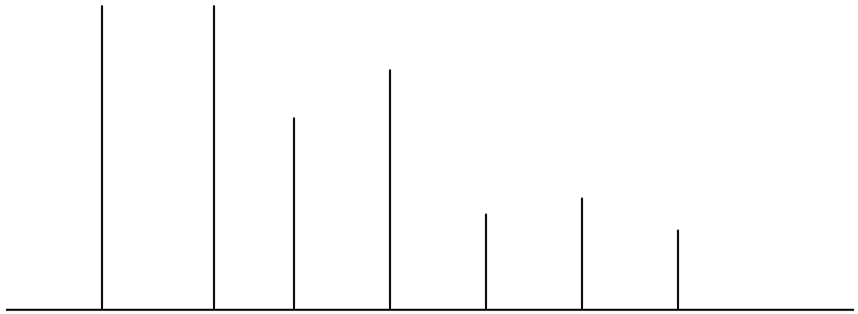
$$2M = 16\pi^2 \langle u_s^2 \rangle \frac{\sin^2\theta}{\lambda^2}$$

- ***Small*** $\theta \rightarrow$ ***Big*** reflections

- e^{-2M} shrinks (***bigger*** effect) with θ (q)



Low Temperature



High temperature

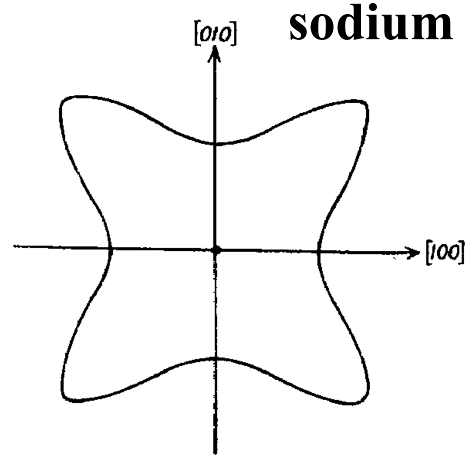
Displacements, u_s depend on ***Debye Temperature*** $\boldsymbol{\theta_D}$ - ***Bigger*** $\boldsymbol{\theta_D}$ $\rightarrow$ ***smaller*** displacements !

TDS makes beautiful patterns reciprocal space

- Iso- intensity contours
  - Butterfly
  - Ovoid
  - Star
- Transmission images reflect symmetry of reciprocal space and TDS patterns

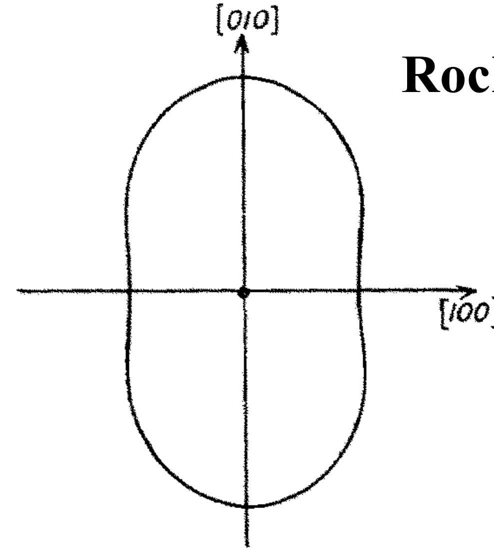
Chiang et al. Phys. Rev. Lett. 83 3317 (1999)

sodium



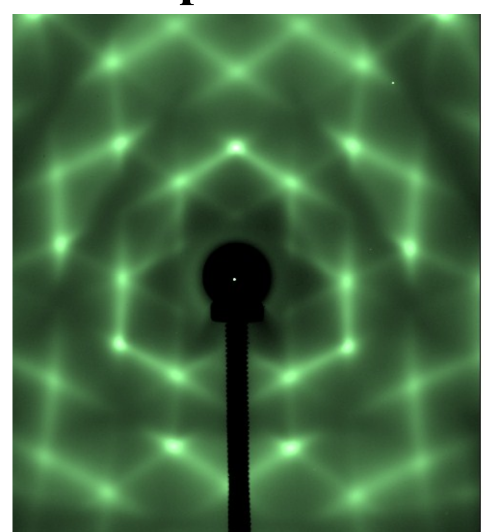
(a) 200 spectrum

Rock salt

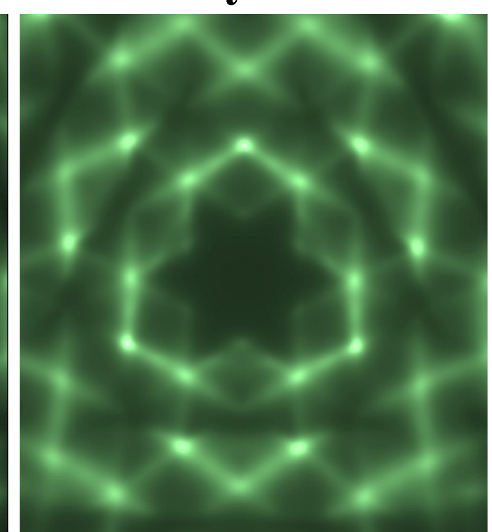


(a) 200 spectrum

Experiment

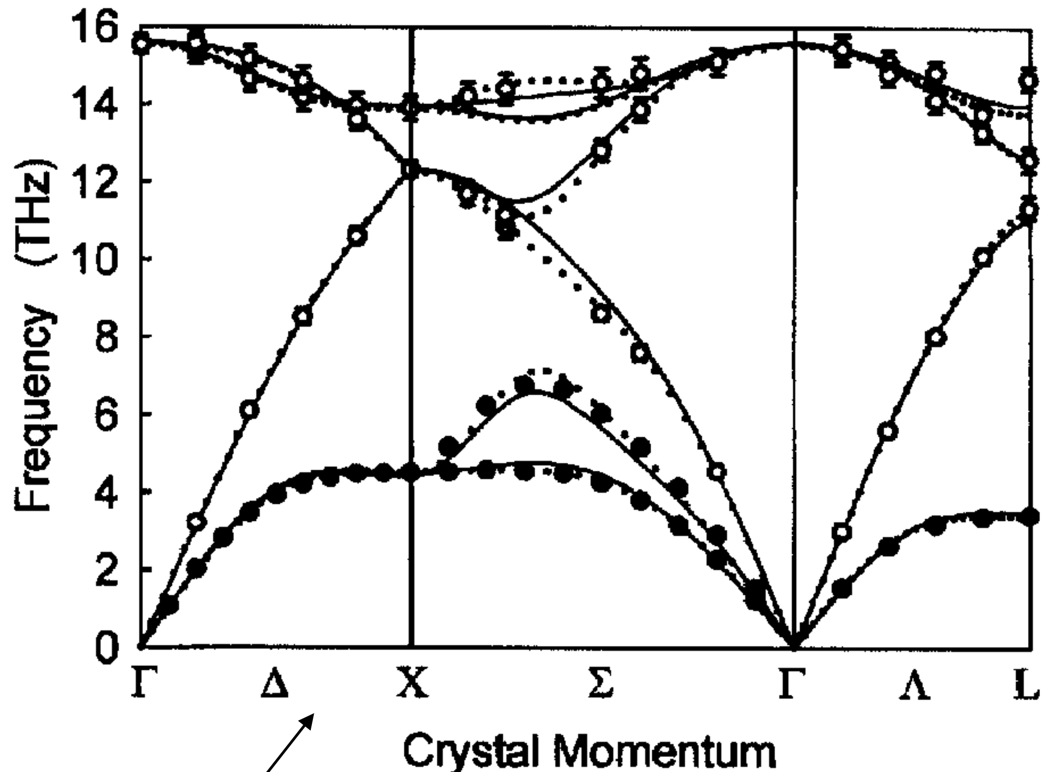


Theory



X-rays *scattering* measurements *infer* phonon dispersion from quasi-elastic scattering

- Phonon energies ***milli-eV***
- Synchrotron based high-E resolution X-ray beamlines can measure phonons *in some cases*
- Emerging area for high-brilliance x-ray sources

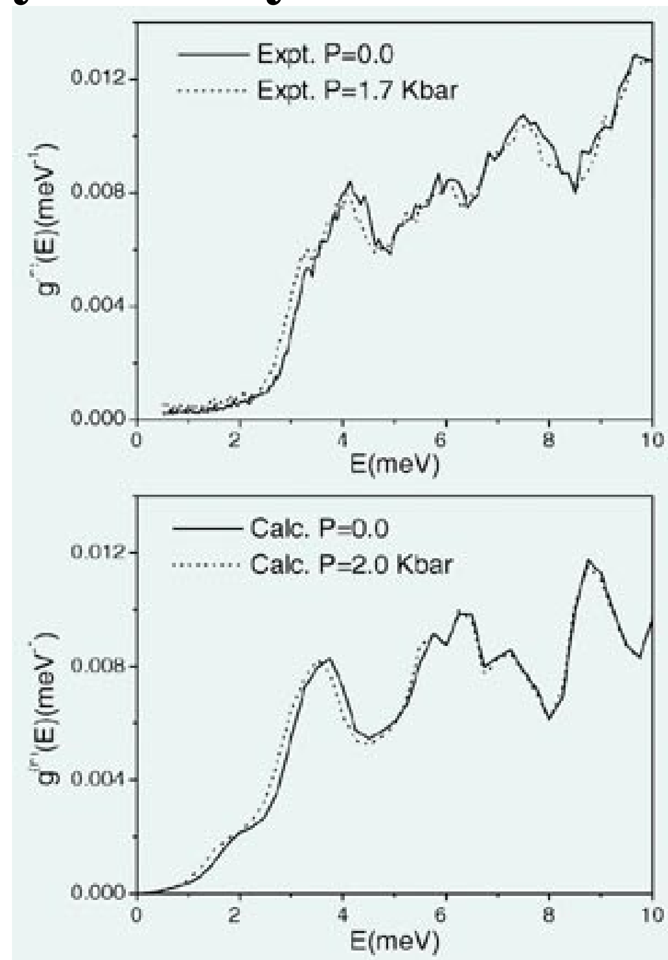


Phonon spectrum gives natural vibration frequencies in different crystal directions!

Inelastic neutron/x-ray scattering directly measures phonon spectra in symmetry directions

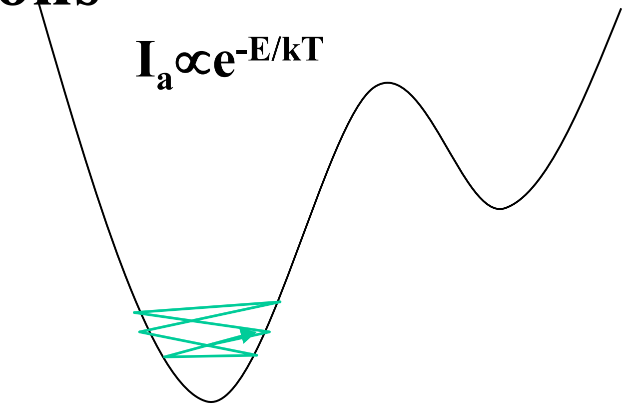
- **Inelastic neutron scattering confirms origins of negative Grüneisen coefficient in cubic ZrW_2O_8 (negative thermal expansion)- disordering phase transition.**

- **Unusual thermal displacements *often associated with phase transitions.***

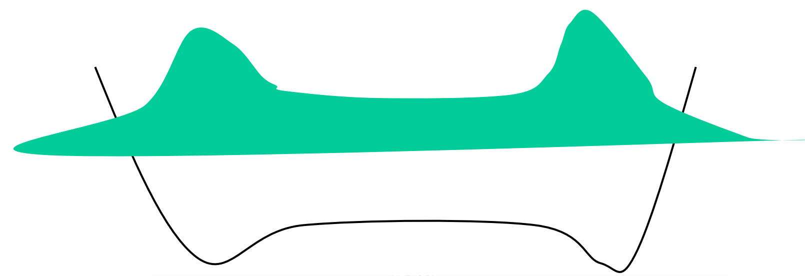


Phonon energies similar to meV neutron energies.

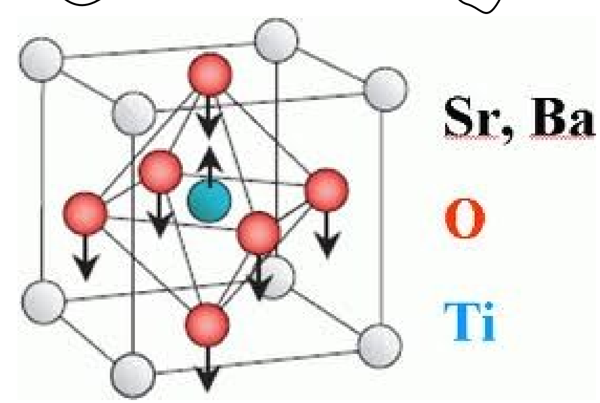
Extra diffuse scattering often observed from materials near phase transitions

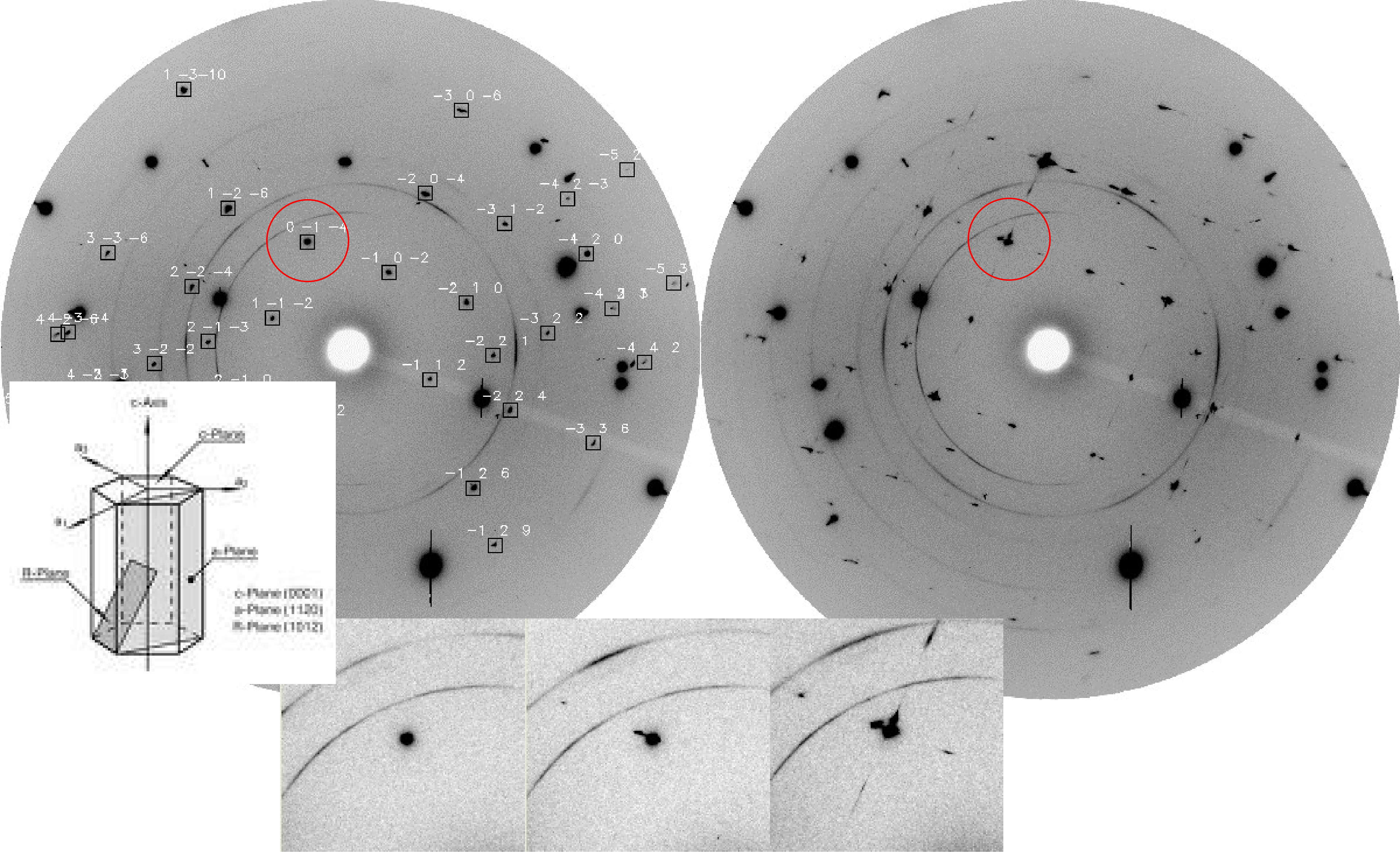


- Distribution of configurations at finite temperature
  - Mixed phases (1st order)

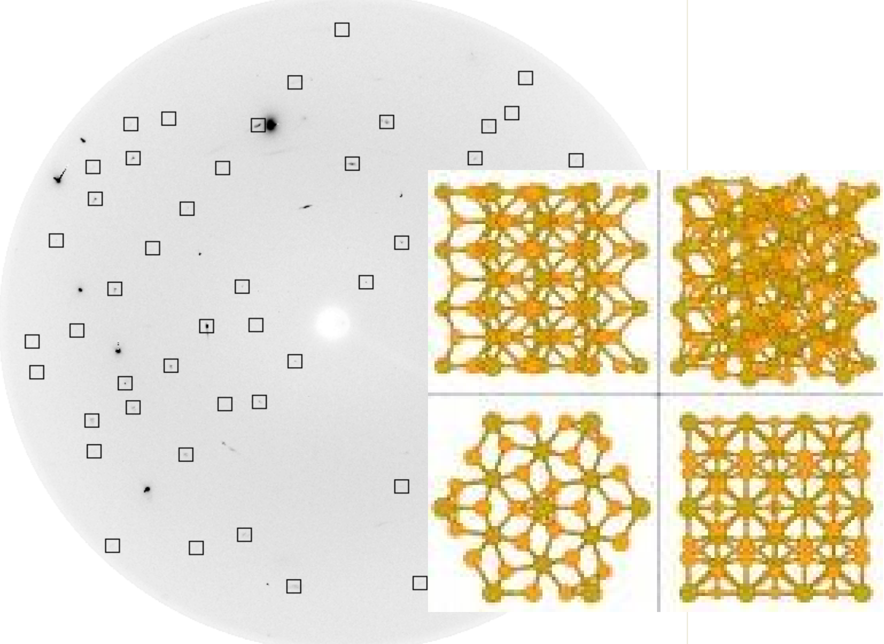


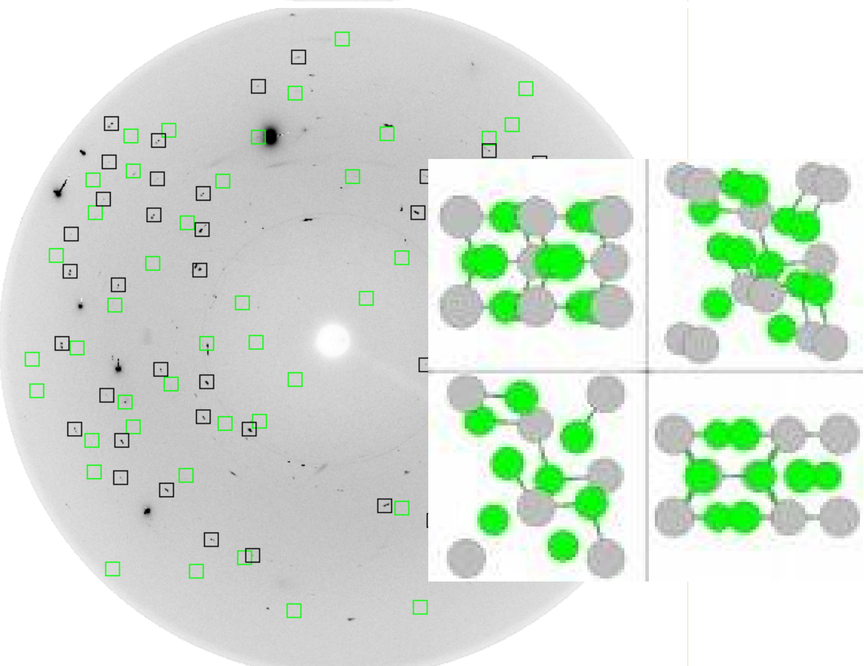
- Extended displacements
- High-pressure
  - higher-co-ordination
  - Longer NN bond distance
  - Smaller volume/atom



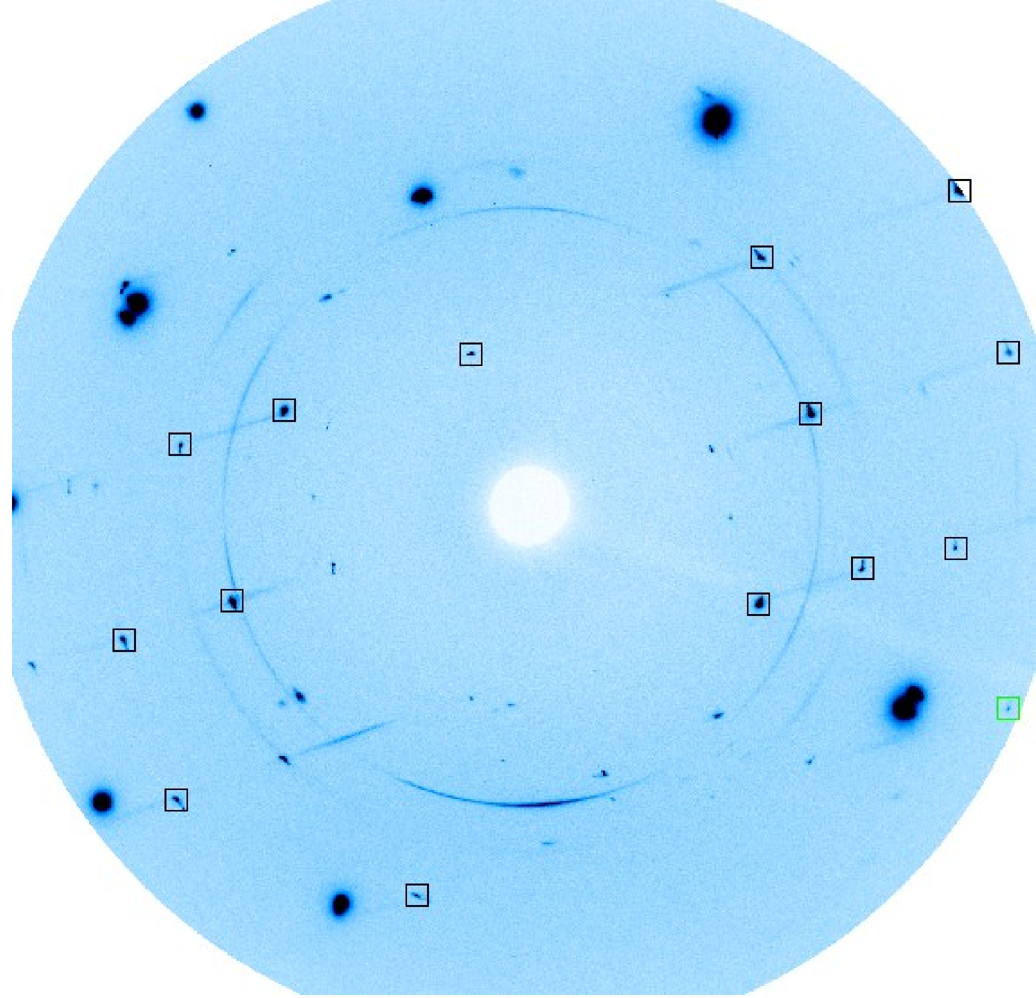


R-3c→I2/a displacive transition observed in a single crystal of Cr_2O_3 at 80 GPA





Complete transformation induced by heating the sample to 2000 K



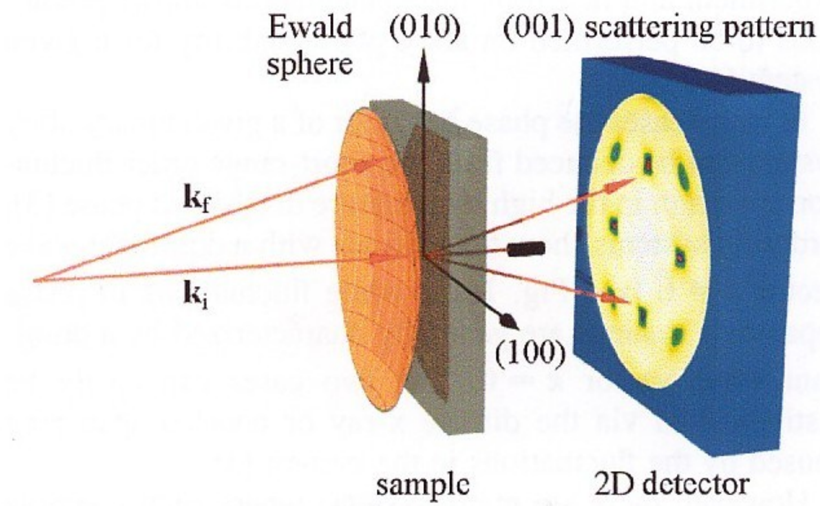
Diffuse scattering before the transformation occurs, heating at~1000 K

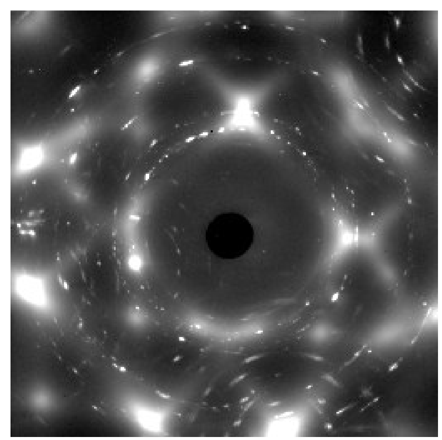
C22→C23 transition in Fe_2P at 10 GPa

Dera et al. (2008) *Gophys. Res. Lett.*, **35**, L10301

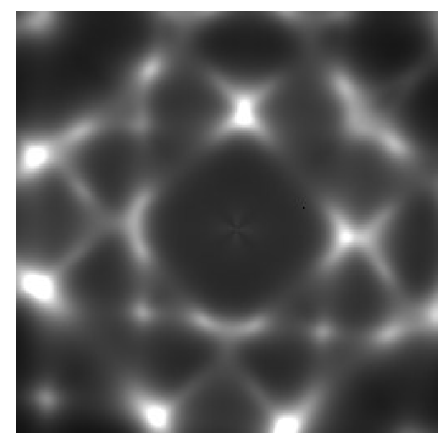
High-energy Synchrotron X-rays are revolutionizing TDS measurements

- Small samples
- Fast (time resolved/ combinatorial)
  - Experiments in seconds rather than days
- Materials that cannot be studied with neutrons





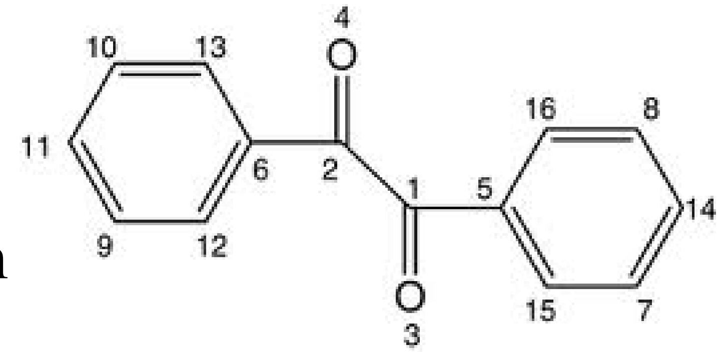
Pu experiment



Pu theory

Neutrons uniquely sensitive to low Z

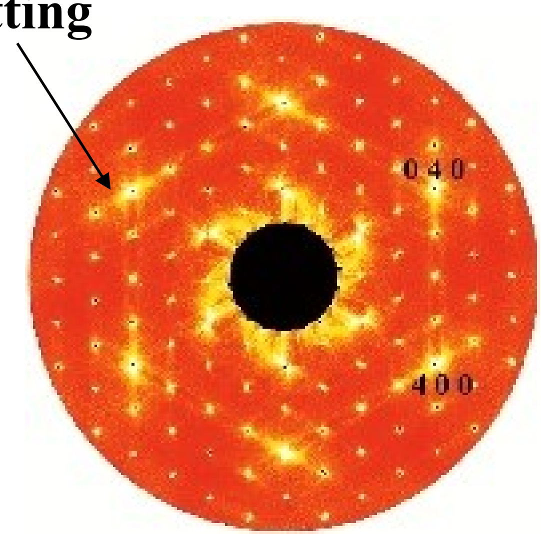
- Deuterium cross section large



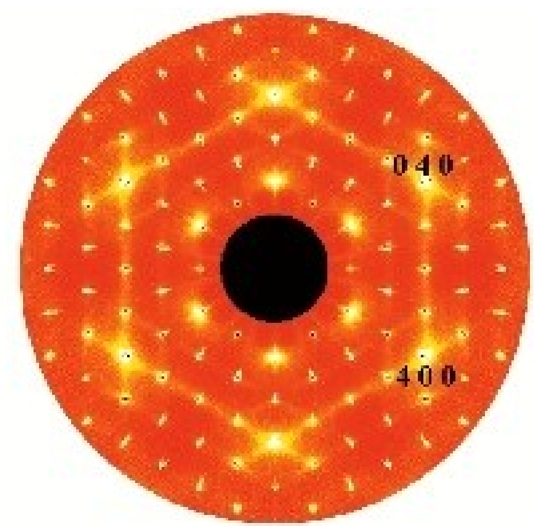
(I)

- Phonon energy comparable to neutron energy
- New insights into dynamics of "molecular crystals" **splitting**

Welberry et al. ISIS



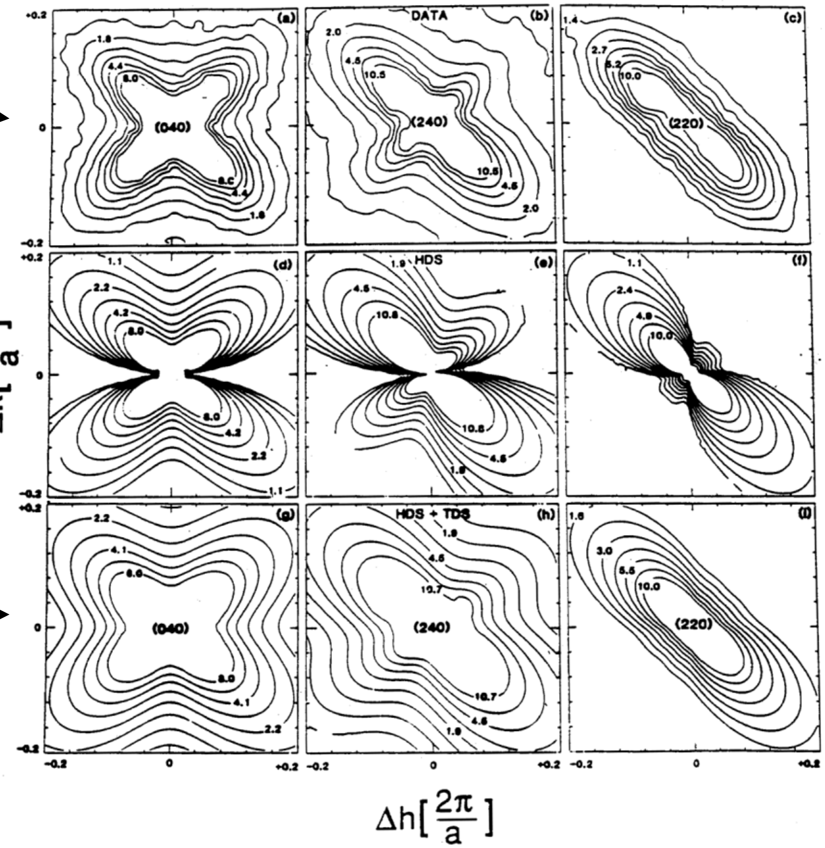
Experiment



Theory

Often TDS mixed with additional diffuse scattering

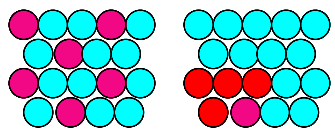
- Experiment
- Strain contribution
- Combined theoretical TDS and strain diffuse scattering



TDS must often be removed to reveal other diffuse scattering

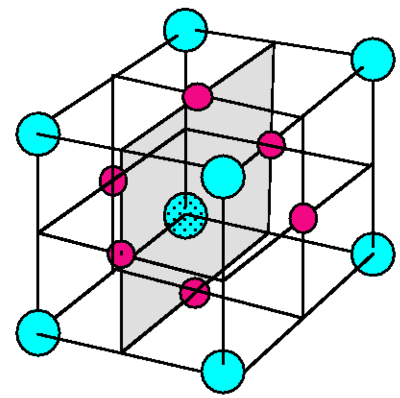
Alloys can have another ***type 1*** defect-***site substitution***

- Long range
  - Ordering (unlike neighbors)
  - Phase separation (like neighbors)

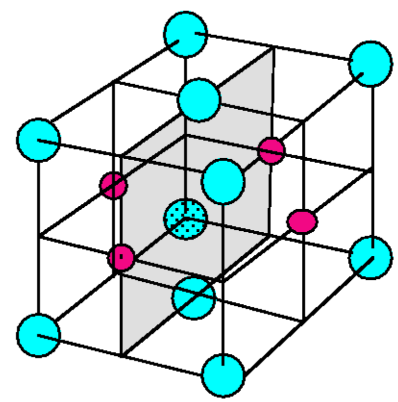


- Short ranged
  - Ordering
  - Clustering (like neighbors)

Each Au has 8 Cu near-neighbors



Cu_3Au
$L1_2$



CuAu
$L1_0$

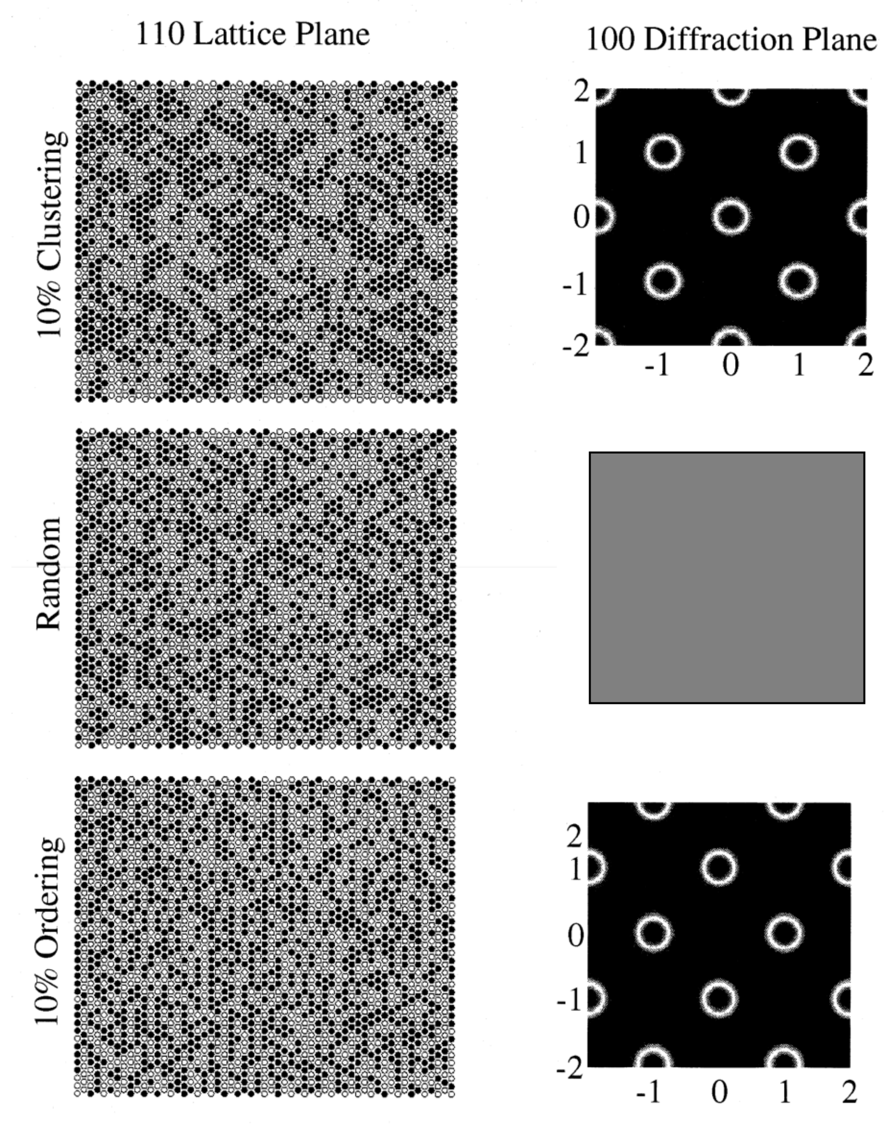
Alternating planes of Au and Cu

Redistribution depends on kind of correlation

Clustering intensity
→ fundamental sites

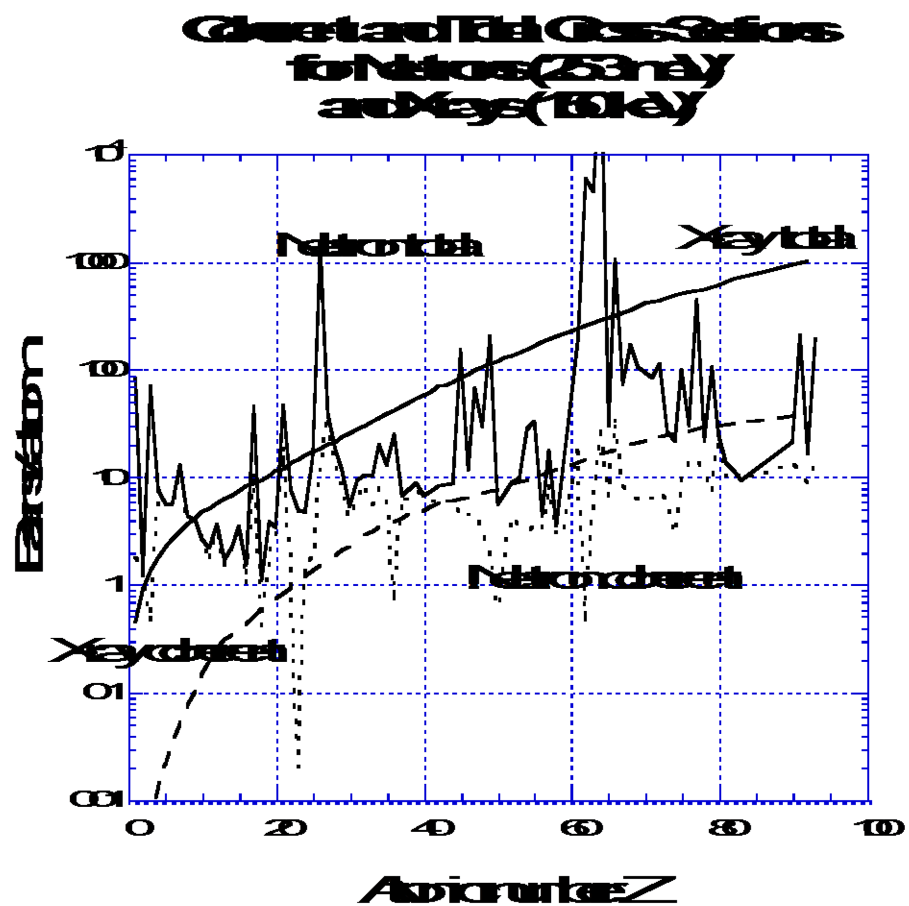
Random causes
Laue monotonic

Short-range ordering
→ superstructure sites



Neutron/ X-rays Complimentary For Short-range Order Measurements

- Chemical order diffuse scattering **proportional to contrast $(f_A-f_B)^2$**
- Neutron scattering cross sections
  - Vary wildly with isotope
  - Can have + and - sign
  - Null matrix
  - Low Z , high Z comparable
- X-ray scattering cross section
  - Monotonic like Z^2
  - Alter by anomalous scattering

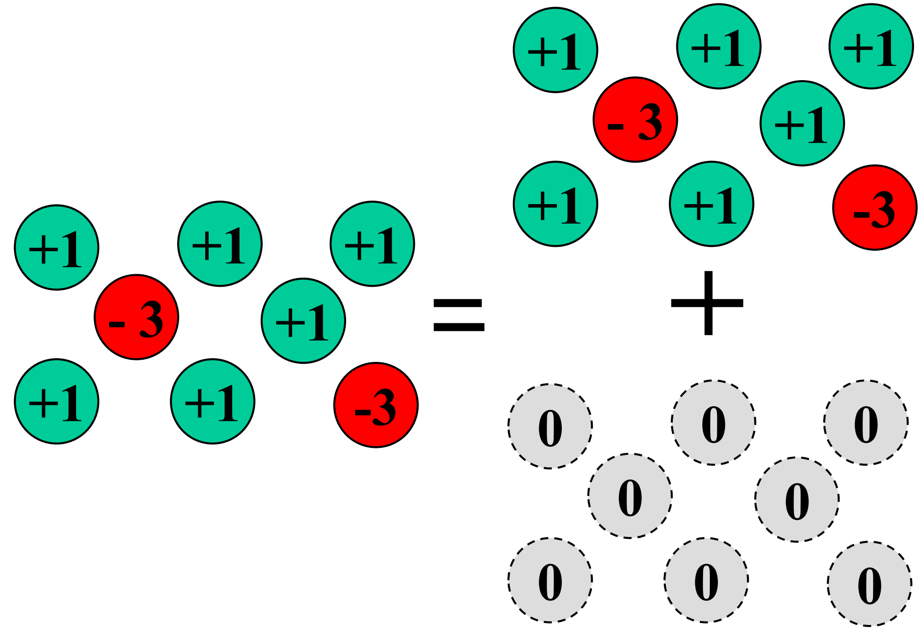


Neutrons can select isotope to ***eliminate*** Bragg scattering

- **Total scattering $c_a f_a^2 + c_b f_b^2 = 3$**

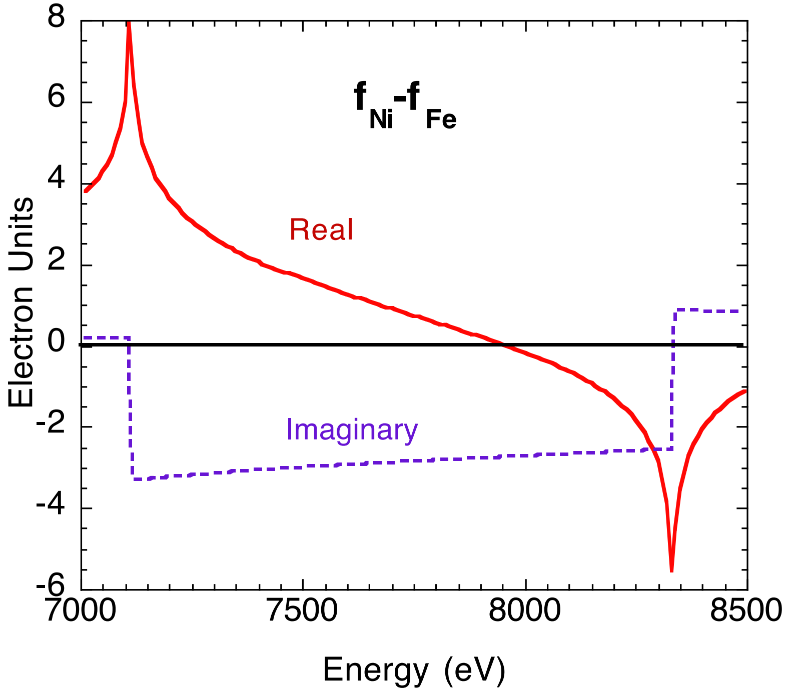
- **Bragg scattering $(c_a f_a + c_b f_b)^2 = 0$**

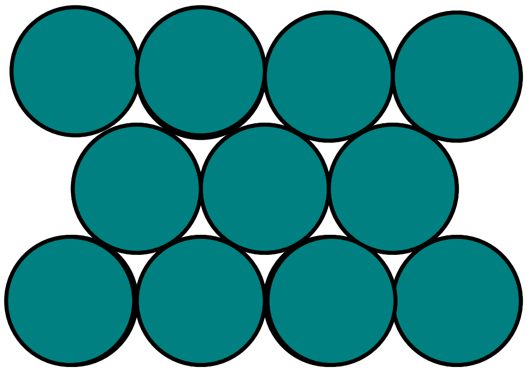
- **Laue (diffuse) scattering**
  $c_a c_b (f_a - f_b)^2 = 3$



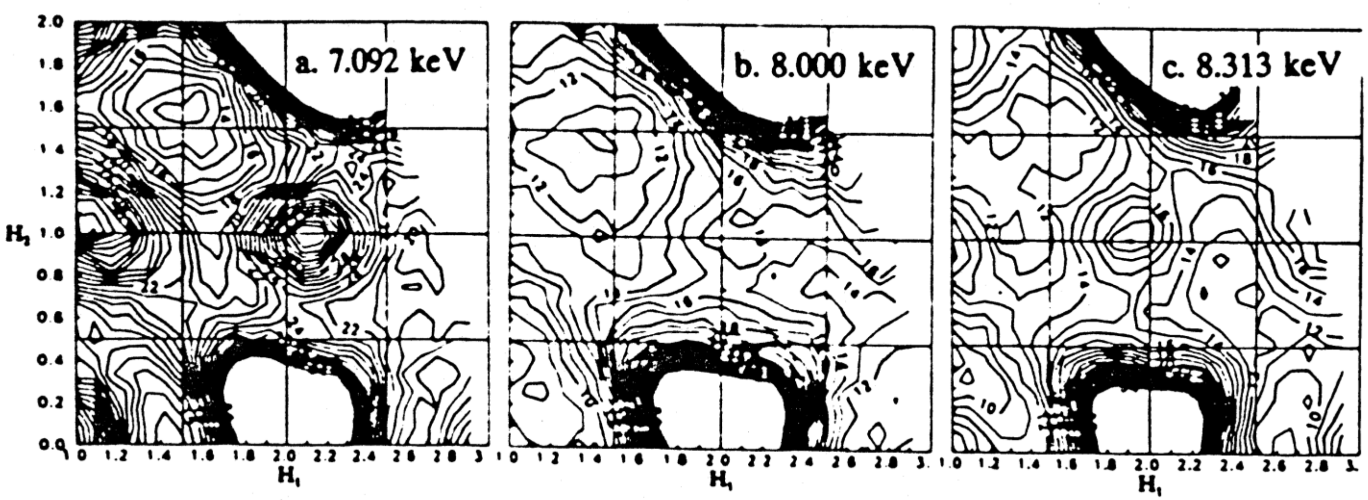
Isotopic purity important as different isotopes have distinct scattering cross sections- <u>only one experiment ever done</u>!

X-ray anomalous scattering can change x-ray contrast





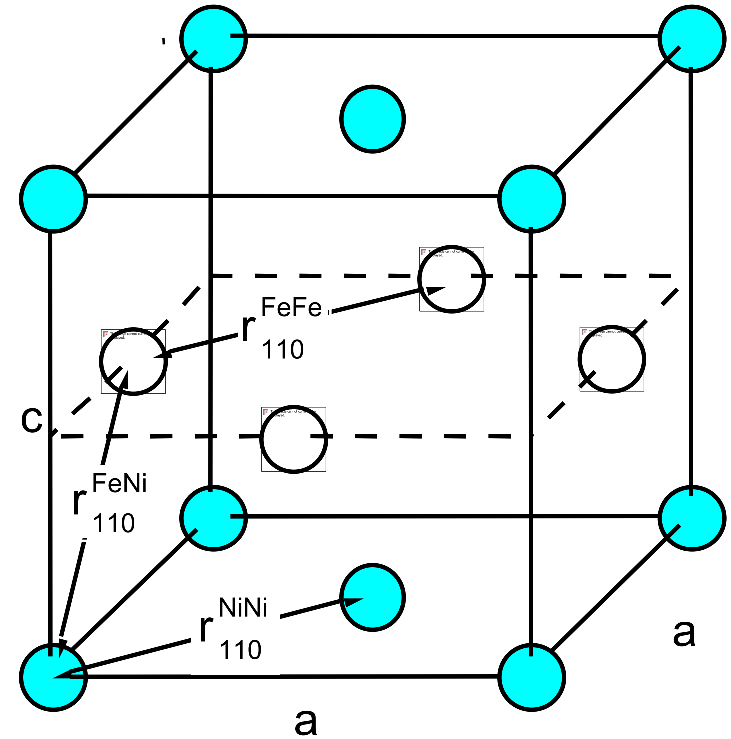
- Chemical SRO scattering scales like $(f_a-f_b)^2$
- Static displacements scale like (f_a-f_b)
- TDS scales like $\sim f_{average}^2$



Atomic size (static displacements) affect phase stability/ properties

- *Ionic materials (Goldschmidt)*
  - Ratio of Components
  - Ratio of radii
  - Influence of polarization

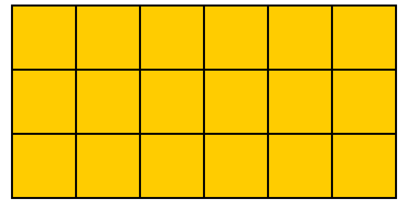
- *Metals and alloy phases (hume-Rothery)*
  - Ratio of radii
  - Valence electron concentration
  - Electrochemical factor

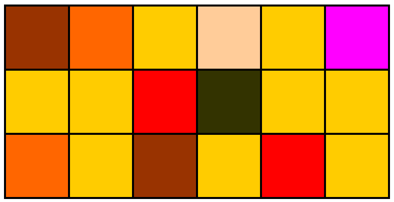


Grand challenge -include deviations from lattice in modeling of alloys

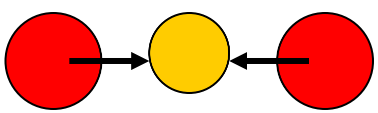
Measurement *and* theory of atomic size are hard!

- Theory- violates repeat lattice approximation- every unit cell different!

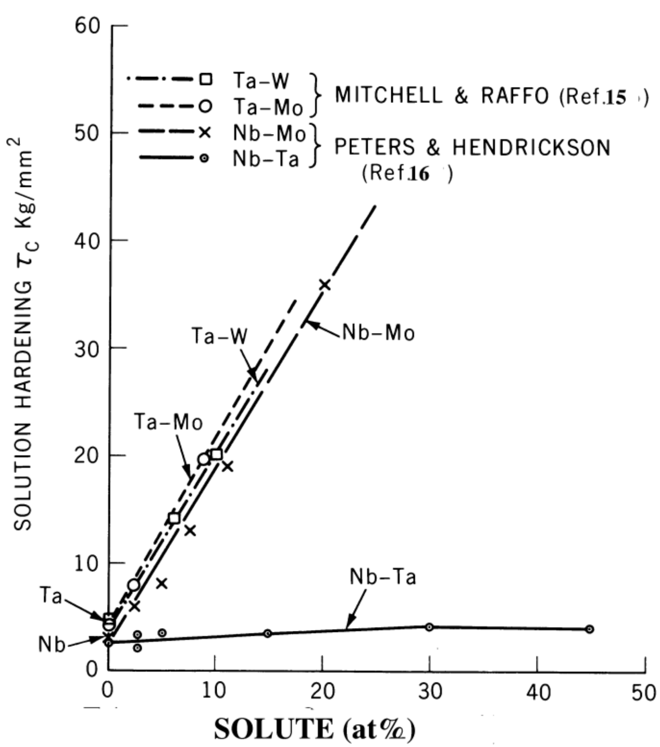




- Experiment
  - EXAFS marginal (0.02 nm) in dilute samples
  - Long-ranged samples have balanced forces

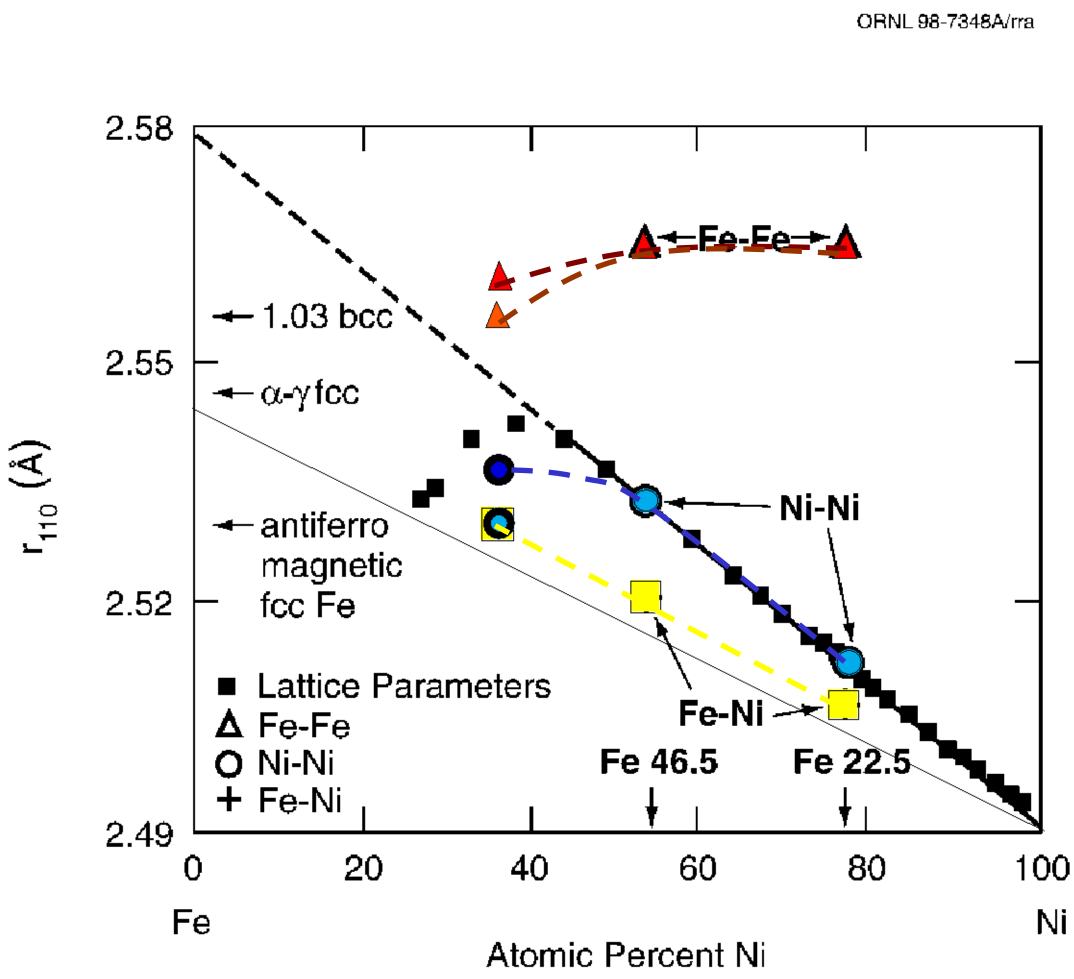


Important!



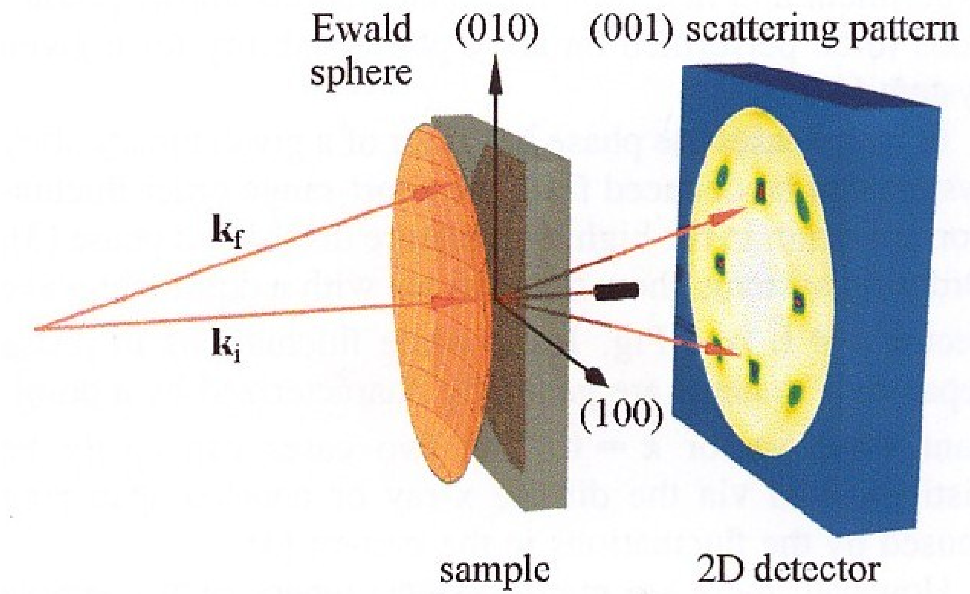
Systematic study of bond distances in Fe-Ni alloys raises interesting questions

- Why is the Fe-Fe bond distance stable?
- Why does Ni-Ni bond swell with Fe concentration?
- Are second near neighbor bond distances determined by first neighbor bonding?

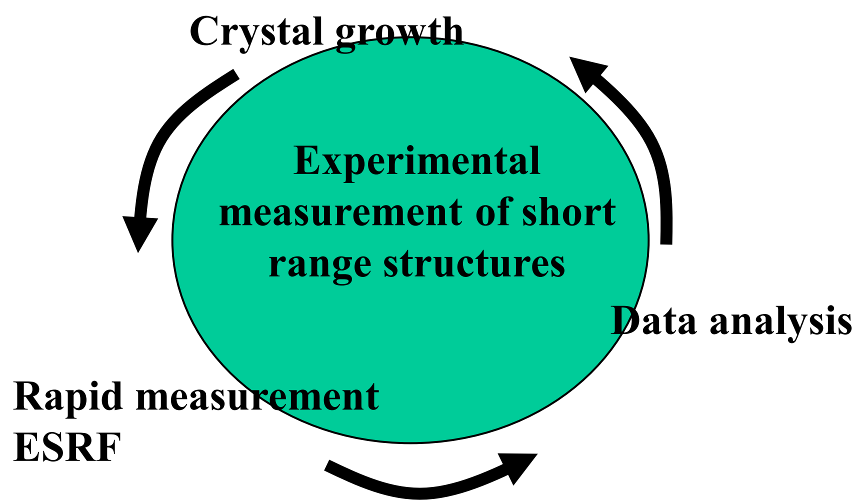


High-energy x-ray measurements revolutionize studies of phase stability

- Data in ***seconds*** instead of ***days***
- Minimum absorption and stability corrections
- New analysis provides direct link to first-principle

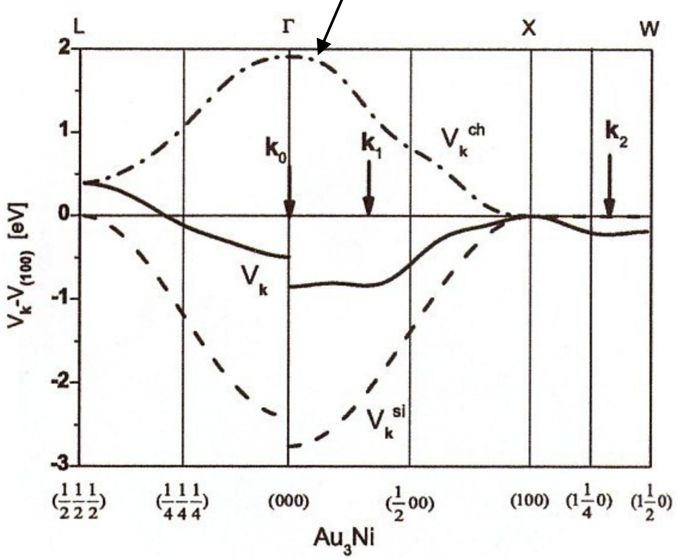


Max Planck integrates diffuse x-ray scattering elements!

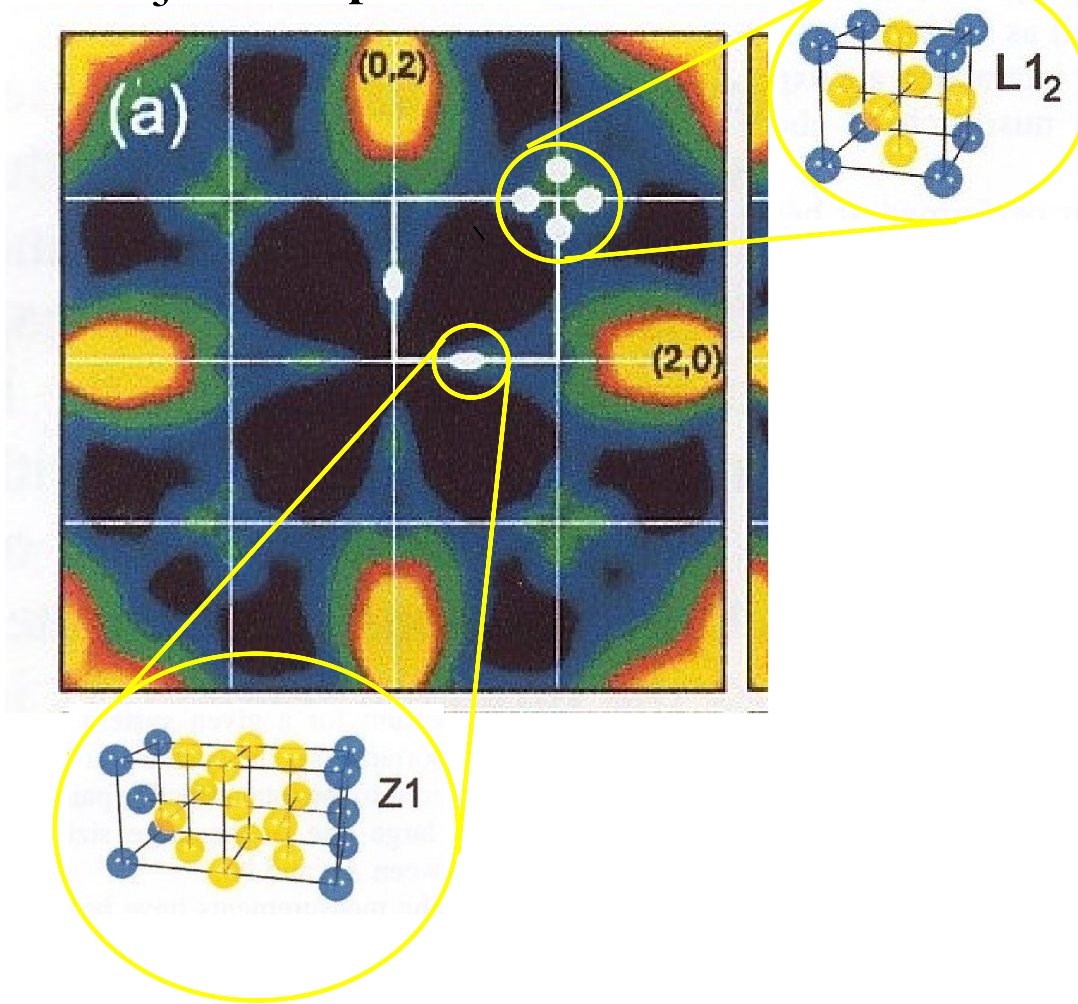


Measurements show competing tendencies to order

- Both $L1_2$ and Z_1 present
- Compare with first principles calculations



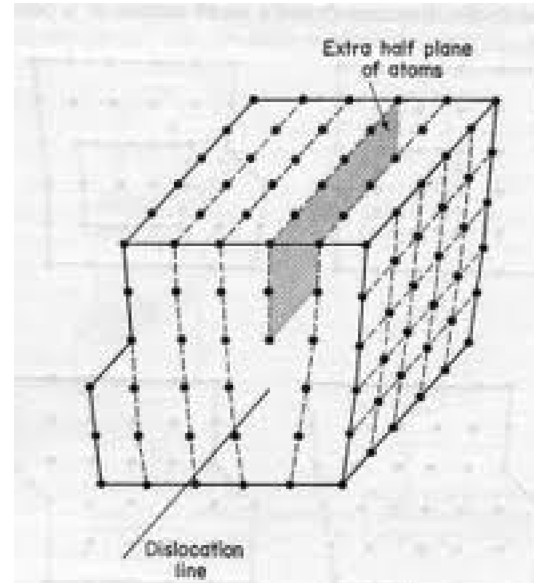
Au$_3$Ni -001 plane



Reichert et al. Phys. Rev. Lett. **95** 235703 (2005)

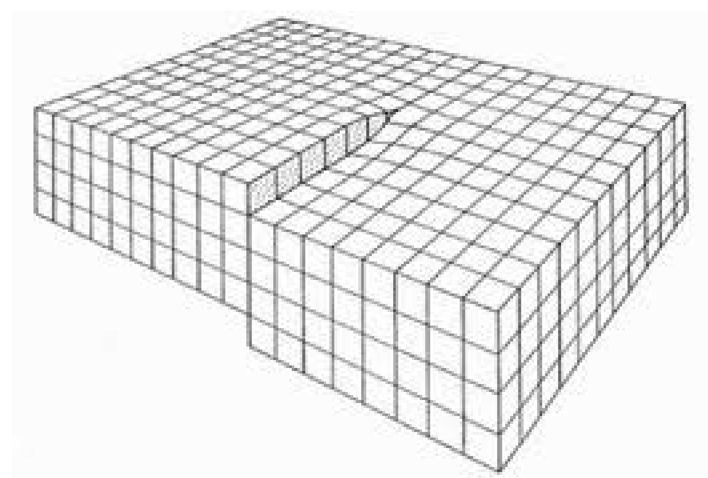
Dislocations -Krivoglaz defect of the second kind

- Unbounded displacement with increased number



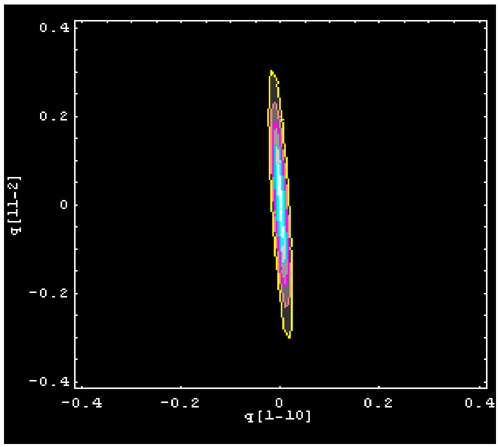
- Broaden Bragg peak

- Fundamental to plasticity

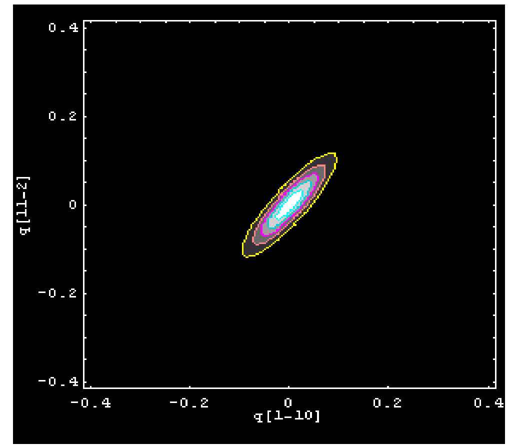


Influence of number and orientation of dislocations can be quantified

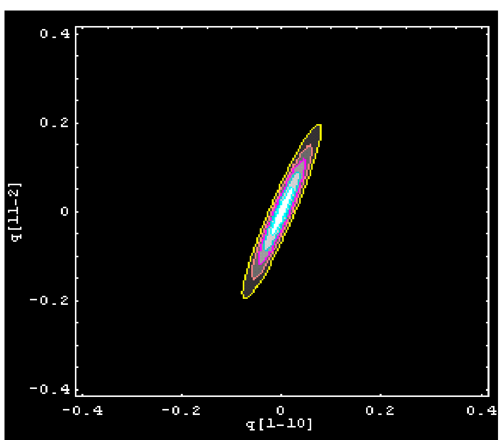
□=[1-2-1], n=[-1-11], b=[101]



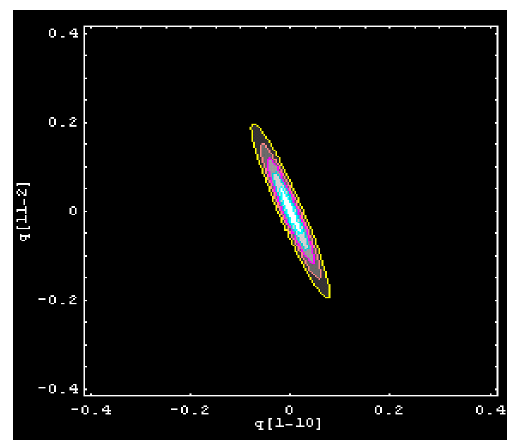
□=[-1-21], n=[-111], b=[101]



□=[-11-2], n=[1-1-1], b=[110]

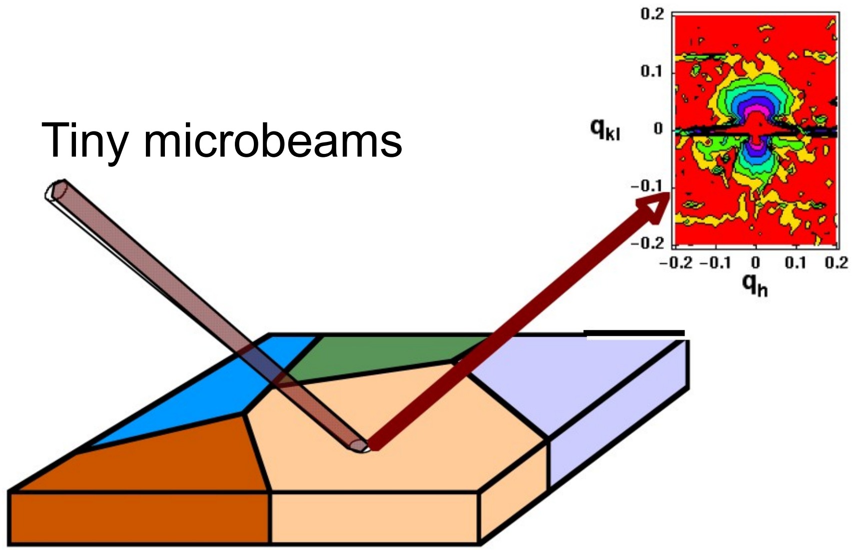


□=[1-1-2], n=[1-11], b=[110]



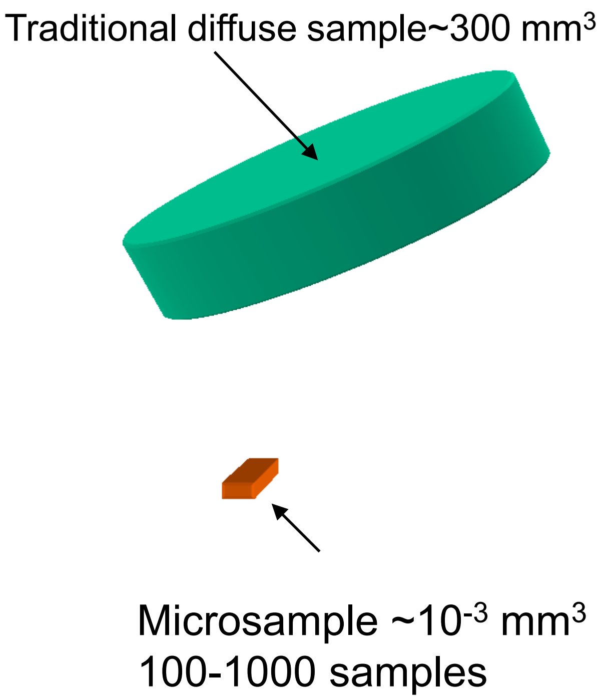
Intense microbeams/area detectors provide new direction in diffuse scattering

- Tiny crysals (20 μm)
  - Natural polycrystals
  - No special sample prep
- Combinatorial
- Dangerous samples



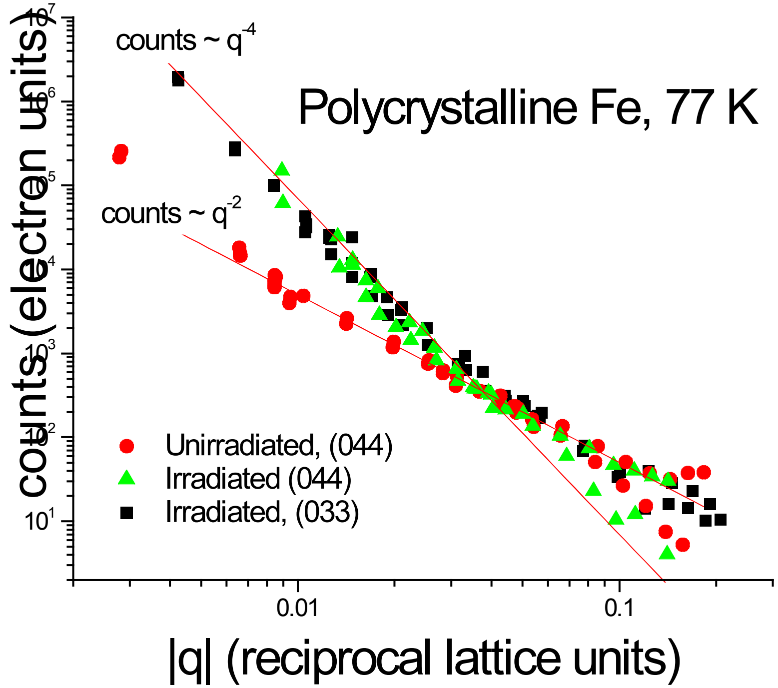
Small irradiated volumes simplify handling/preparation

- Activity ~volume (10^{-5})
- Much less waste (10^{-7})
- Polycrystalline samples easier obtain- *closer to real materials*



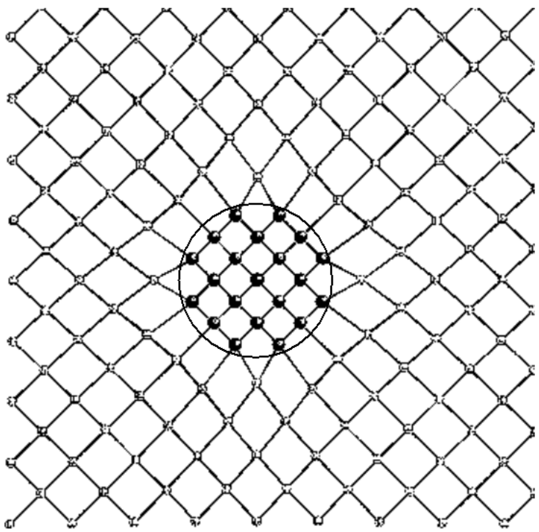
Diffuse microdiffraction holds promise for irradiated materials

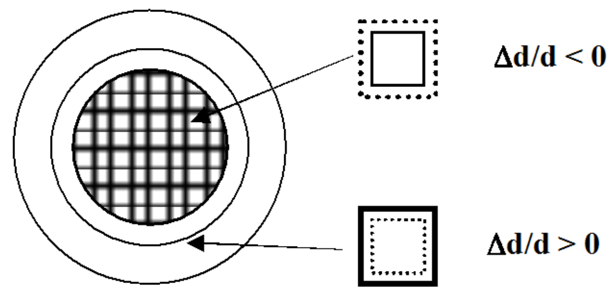
- Powerful single crystal techniques applied to polycrystals
- ~4-6 Orders of magnitude lower activity
  - Safer/lower backgrounds
- Cryocooled samples to study initial defects
- New information about point/line/mesoscale defect interactions

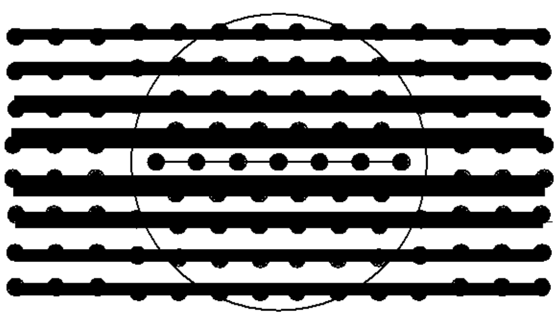


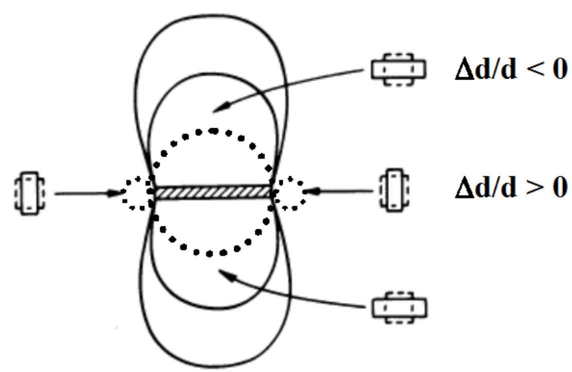
Successful demonstration experiments!

Vacancies, interstitials, small dislocation loops, coherent precipitates are additional type 1 defects



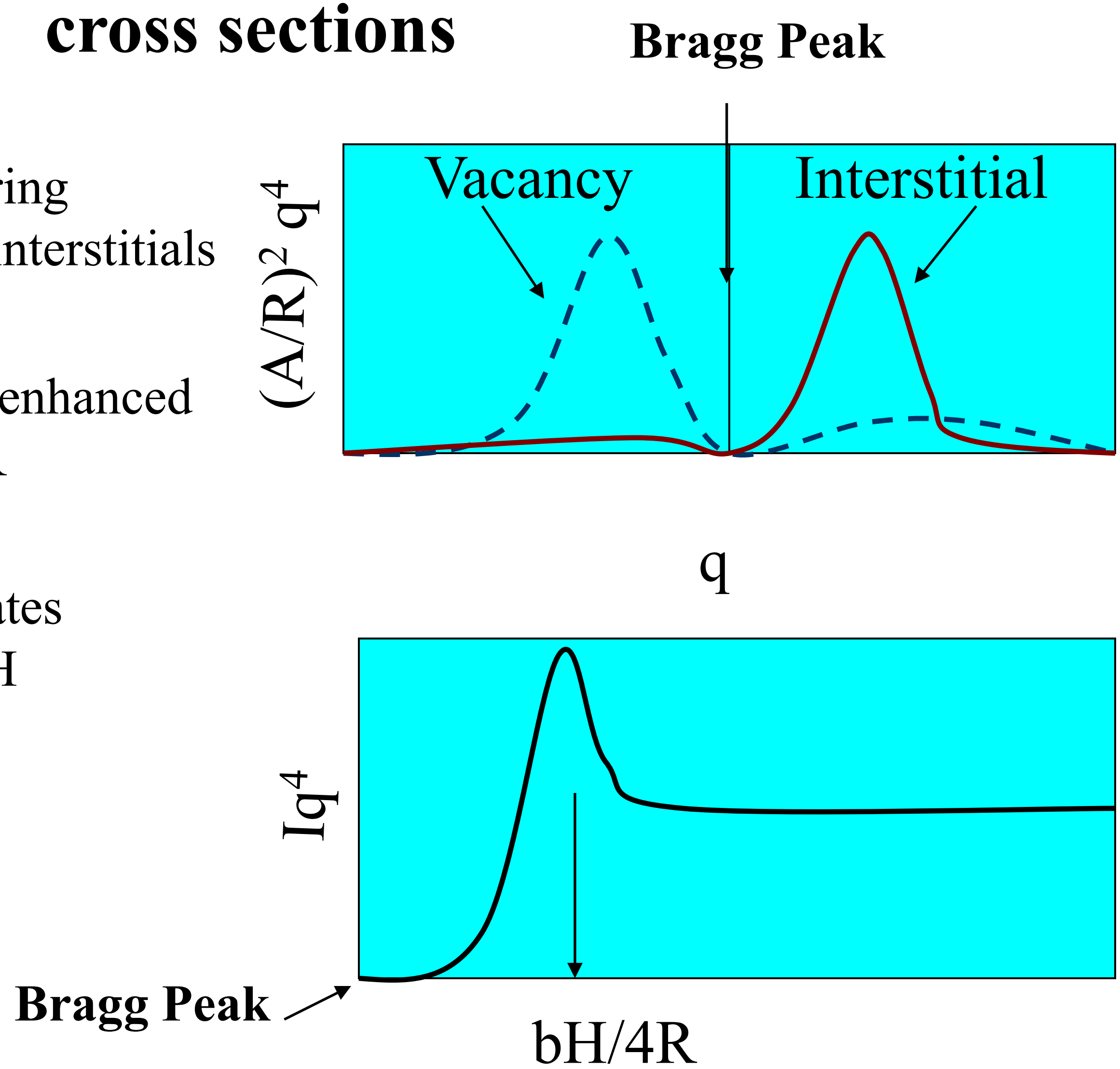






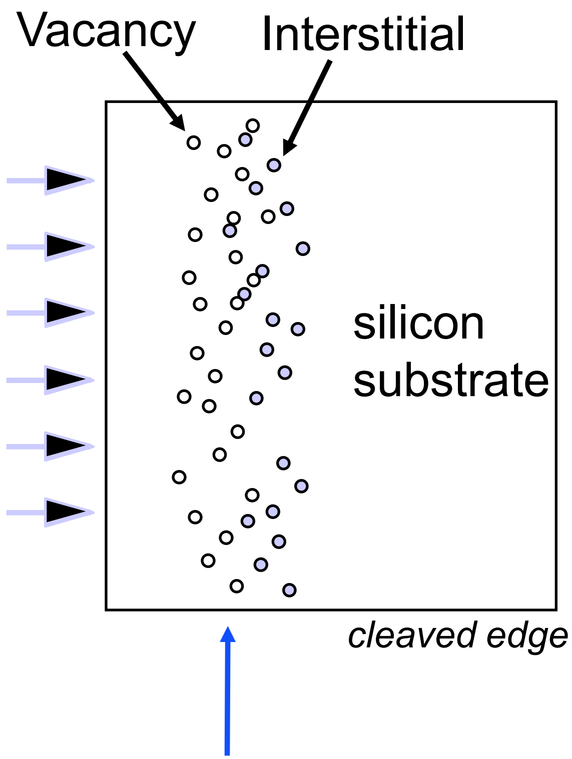
Numerical calculations determine quantitative cross sections

- Sign of diffuse scattering reverses for vacancy/interstitials
- For interstitial loops- enhanced scattering at q=bH/4R
- For coherent precipitates enhancement at q=-εH



Micro-diffuse scattering applied to High Energy, Self-Ion Implantation in Si

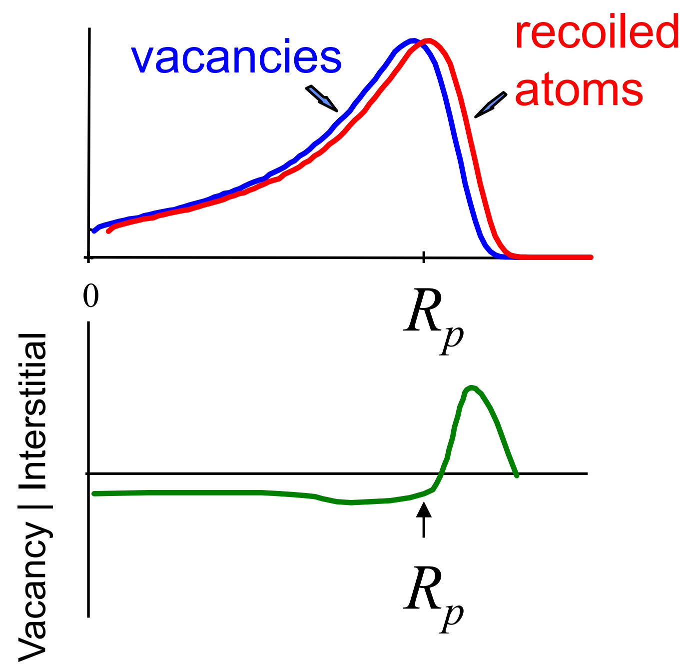
1-10 MeV Si^{+}

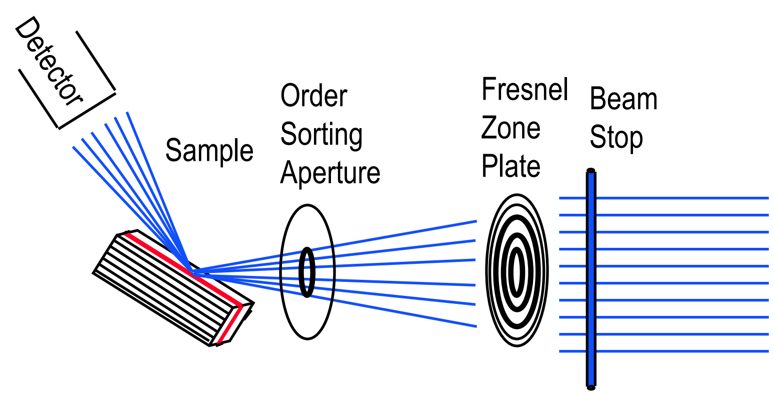


X-ray Microbeam

- cleave sample in cross-section
- translate to probe depth dependence

Spatial separation of recoils and vacancies due to momentum transfer

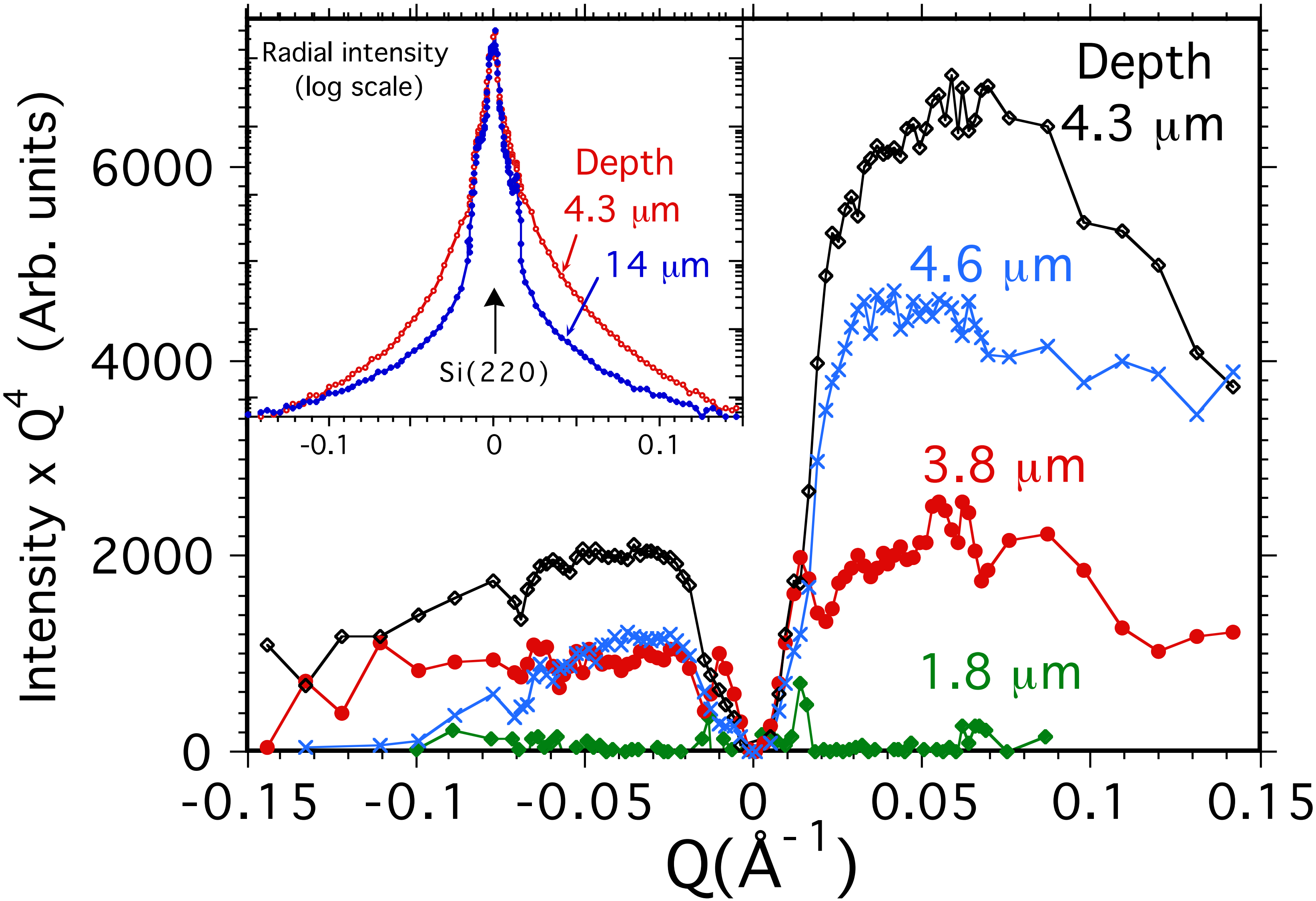




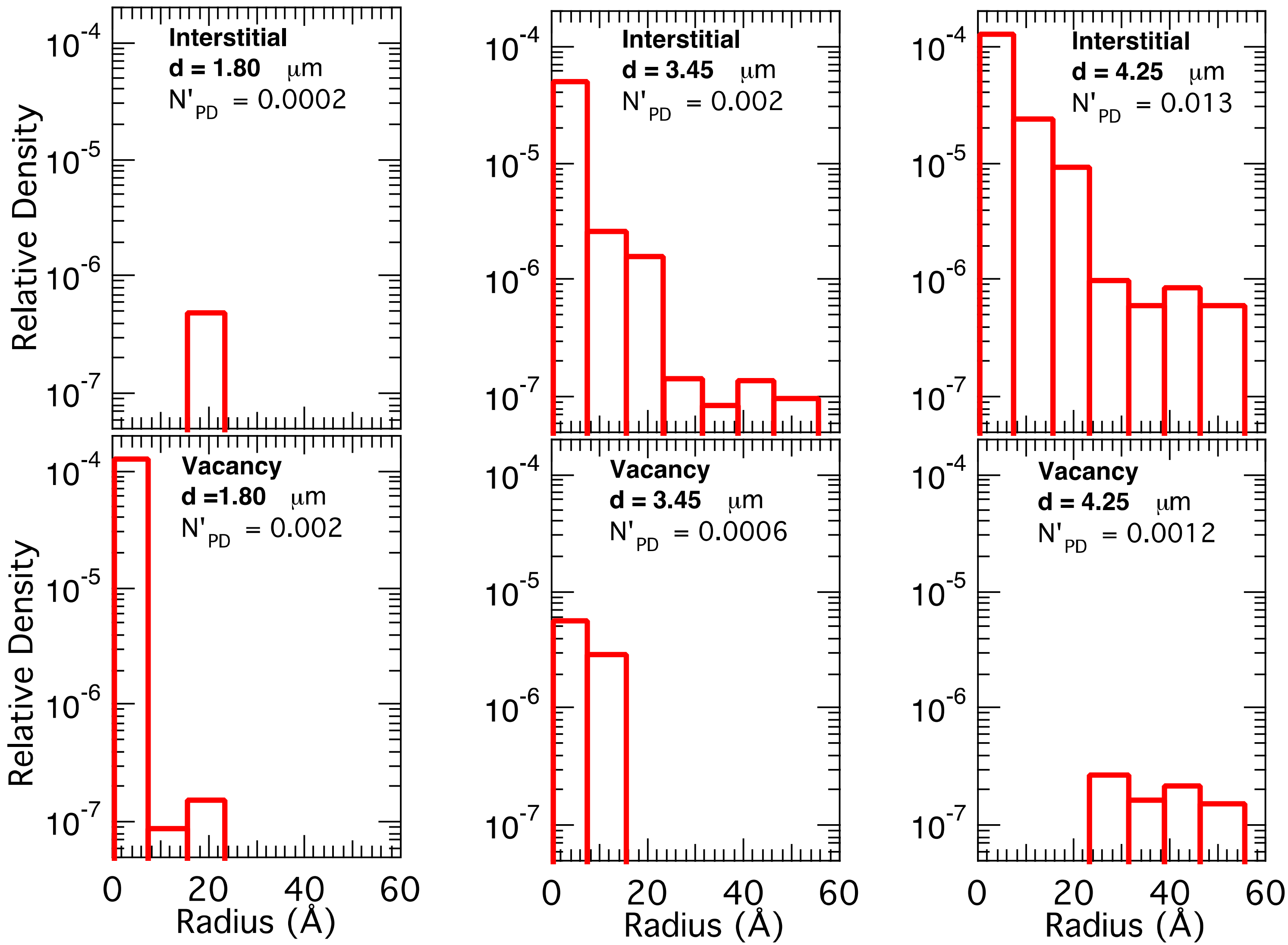
Yoon, Larson, Tischler, Haynes

X-ray Diffuse Scattering

Huang theory ⇒ for $Q \ll 1/R$, $I \propto Kb\pi R^2/Q^4$

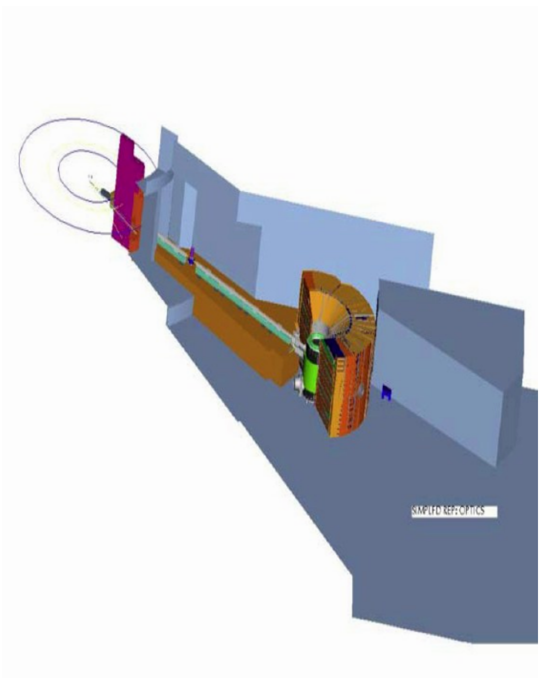


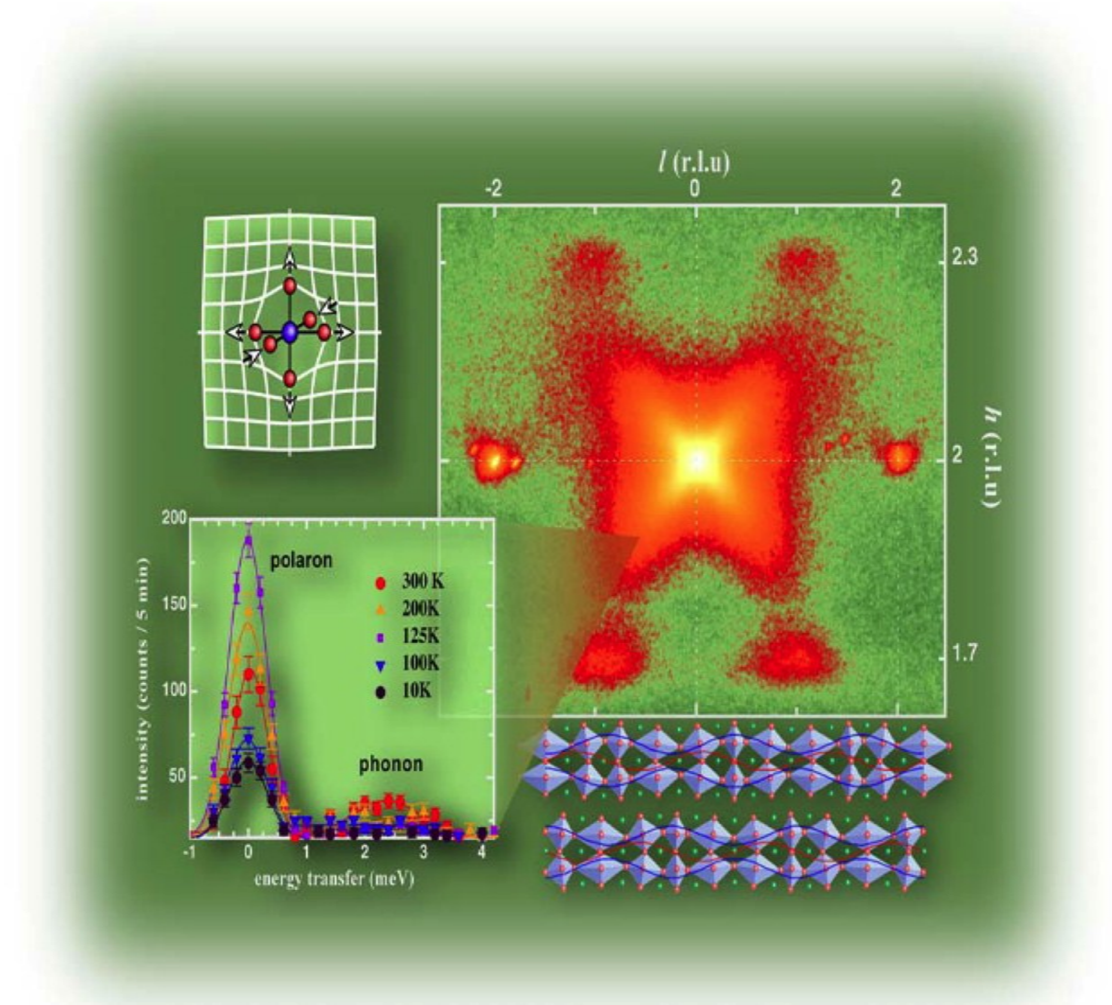
Depth Dependence of Size Distributions for Ion-Implanted Si



Corelli SNS beamline specialized for diffuse scattering with elastic Discrimination

- Complex disorder and short-range correlations

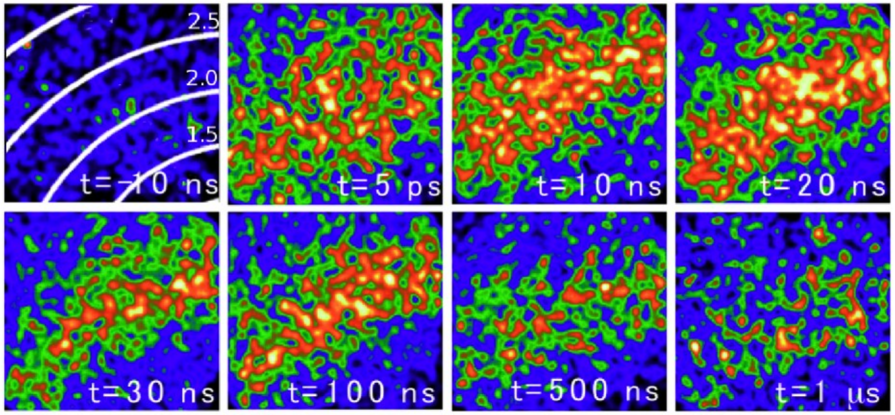




X-ray diffuse scattering at Femtosecond Resolution

- **Ultra-brilliant LCLS opens new experimental possibilities**

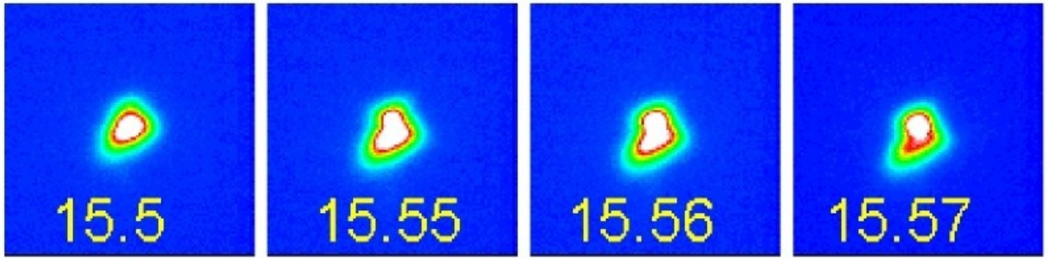
- **Transient behaviors at femtosecond time scales demonstrated.**



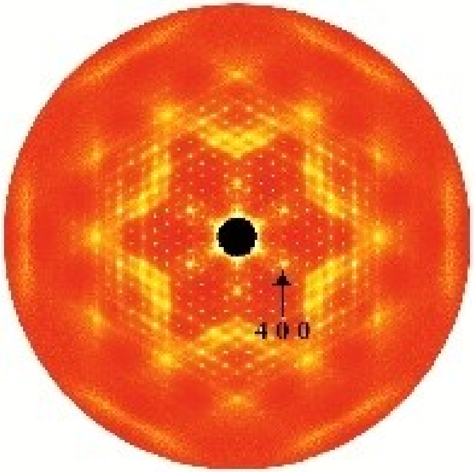
Lindenberg et al. PRL 100 135502 (2008)

New directions in diffuse scattering

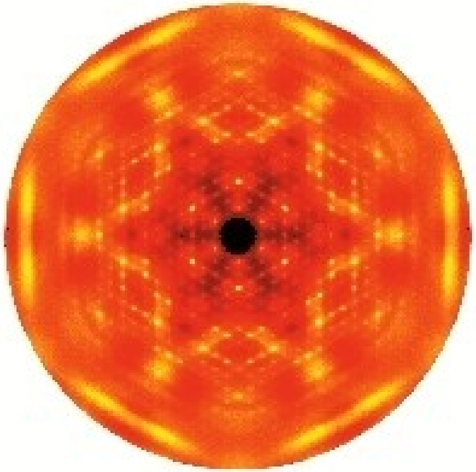
- High-energy x-ray
- Microdiffuse x-ray scattering
  - Combinatorial
  - Easy sample preparation



- Diffuse neutron data from every sample
- Interpretation more closely tied to theory
  - Modeling of scattering x-ray/neutron intensity



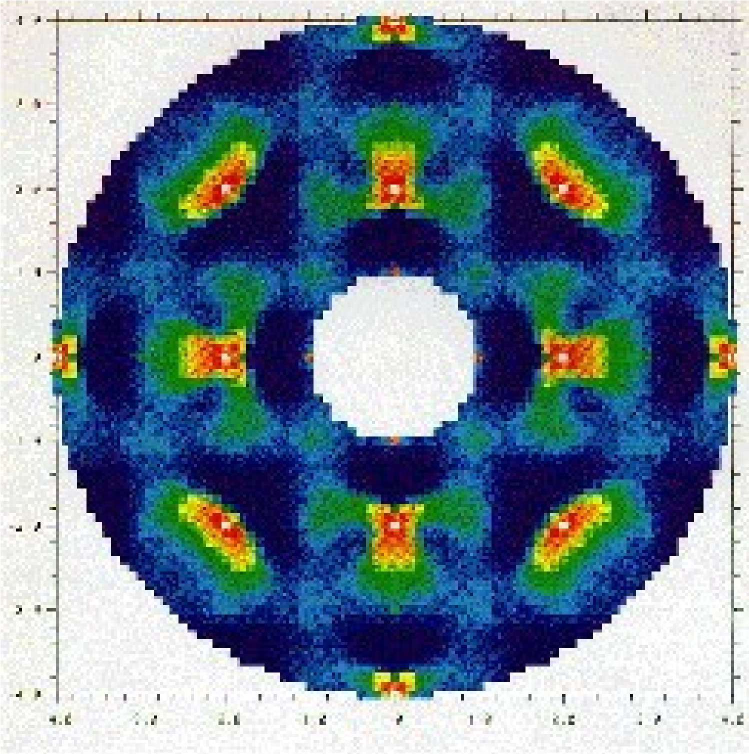
Experiment



Model

Intense synchrotron/neutron sources realize the promise envisioned by pioneers of diffuse x-ray scattering

- M. Born and T. Von Karman 1912-1946- *TDS*
- Andre Guiner (30' s-40' s)-*qualitative size*
- I. M. Lifshitz *J. Exp. Theoret. Phys. (USSR)* **8** 959 (1937)
- K. Huang *Proc. Roy. Soc.* **190A** 102 (1947)-*long ranged strain fields*
- J. M Cowley (1950) J. Appl. Phys.-*local atomic size*
- Warren, Averbach and Roberts *J. App. Phys* **22** 1493 (1954) -*SRO*
- Krivoglaz *JETP* **34** 139 1958 *chemical and spatial fluctuations*



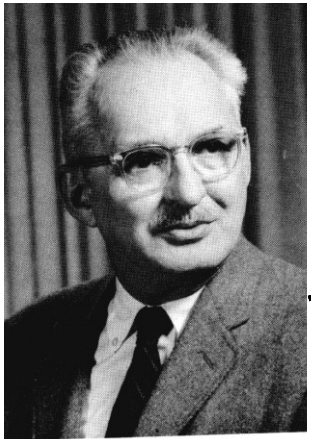
Other references:

- X-ray Diffraction- B.E. Warren Dover Publications New York 1990.
- http://www.uni-wuerzburg.de/mineralogie/crystal/teaching/dif_a.html
- Krivoglaz vol. I and Vol II.

Diffuse scattering done by small community

A. Gunier

- Warren school



S. Cowley, *Arizona St.*

Bernie Borie, *ORNL*

Jerry Cohen, *Northweste*

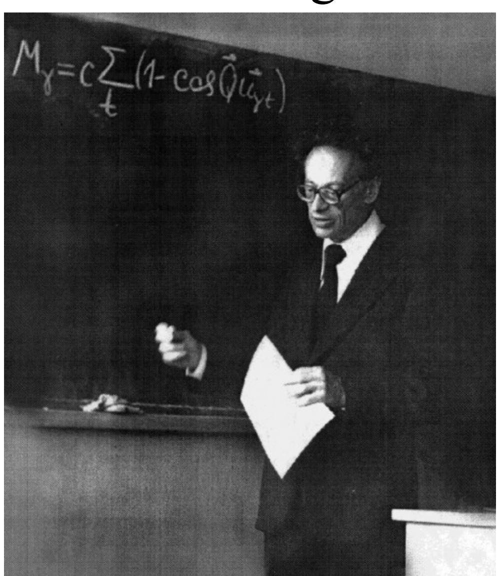
B. Schoenfeld, ETH Z

W. Schweika, K

Simon Moss, *U*

rks

- Krivoglaz school



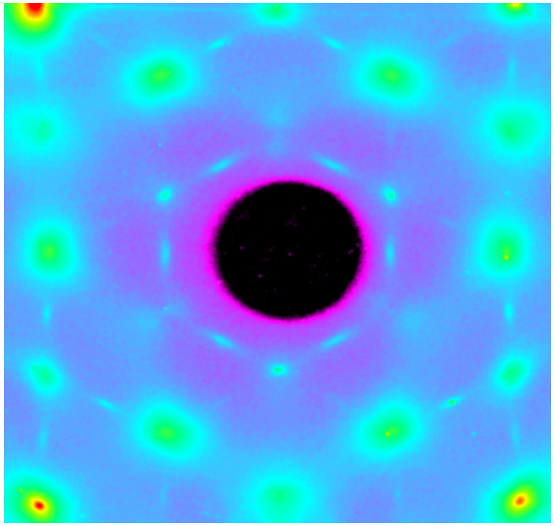
Peisl, *U. München*

H. Reichert, *Max Planck*

Gitgarts, *Minsk*

Rya Boshupka, *IMP*

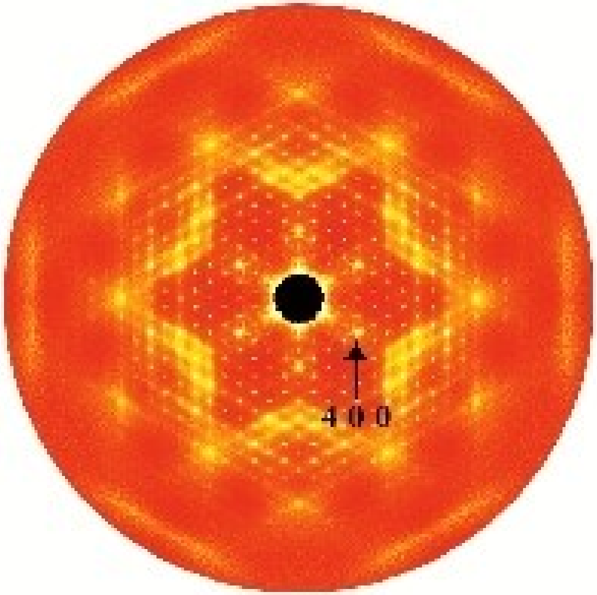
Diffuse scattering song



Come eager young scholars- so tender and new
I' ll teach you diffraction- what I says mostly true
Between the Bragg Peaks lies a world where you see
Fluctuations and defects- they stand out plane-ly

Chorus
For its dark as a dungeon between the Bragg peaks
But here in the darkness- each defect speaks
It gathers- from throughout- reciprocal space
And re-distributes all over the place.

Between the Bragg peaks - one thing that we see
Is TDS on our CCD
Intensity totals are conserved- you can' t win
It steals from the Bragg peaks that stay very thin



Substitutional alloys can cause quite a stir
The shorter the length scale the greater the blur
With care you can find out the bond length between
Each atom pair type-the measurements clean

Dislocations and other- type 2 defects
Destroy the Bragg peaks -they turn them to wrecks
But near the Bragg peaks- you still can see
Intense diffraction continuously

Many -are- the defects you find
Between the Bragg peaks where others are blind
So go tell your friends and impress your boss
You' ve new understanding -with one hours loss